THE POLYMERIZATION OF DICYCLOPENTADIENE: AN INVESTIGATION OF MECHANISM

By

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To my teachers -

for turning me on to science

and convincing me to carry the torch

for the next leg of the race.

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THE POLYMERIZATION OF DICYCLOPENTADIENE: AN INVESTIGATION OF MECHANISM

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Chairman: Professor Kenneth B. Wagener
Major Department: Chemistry

The generally accepted mechanism for the formation of polydicyclopentadiene is ring-opening metathesis polymerization (ROMP) of the strained norbornene moiety, followed by subsequent ROMP of the fused cyclopentene. This work details mechanistic investigations of the polymerization of dicyclopentadiene with a classical metathesis catalyst, WCl_6/Et_2AlCl (1), and three preformed alkylidenes, Schrock's molybdenum catalyst, $Mo(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr)(CHC(CH_3)_2Ph)(OCCH_3(CF_3)_2)_2$ (2), and Grubbs' ruthenium catalysts, $Ru(CHPh)Cl_2(PR_3)_2$, where R = cyclohexyl (3) or phenyl (4).

Utilizing the model compounds 8,9-dihydrodicyclopentadiene (5) and 5,6-dihydrodicyclopentadiene (6), insight was gained into the mechanism that leads to crosslinked polydicyclopentadiene. Compound 5 underwent facile metathesis, yielding a ring-opened product upon exposure to either classical catalyst 1 or molybdenum catalyst 2. Compound 6 appeared to be nonreactive with molybdenum alkylidene 2 and ruthenium catalysts 3 and 4, yet reacted via an olefin addition process when subjected to

catalyst 1. Additionally, dimers and trimers of compound 6 were formed from heating in the absence of any catalyst.

Linear polydicyclopentadiene was generated in solution with molybdenum catalyst 2. However, at higher concentrations of monomer, insoluble material was formed. When heat was removed from the polymerization of dicyclopentadiene through dilution or by cooling the solution, soluble linear polymer was formed. This finding supported the theory that a thermally catalyzed olefin addition process is at least partly responsible for the crosslinking reaction of polydicyclopentadiene.

Polymerization of dicyclopentadiene (9) with ruthenium alkylidenes 3 and 4 resulted in the formation of insoluble polymers, regardless of the concentration of the solutions. This result was inconsistent with the experiments with compound 6 and the ruthenium catalysts, where no metathesis was observed. These studies indicated that chemistry other than metathesis occured when the ruthenium alkylidenes were employed.

All attempts to crosslink oligomers of linear polydicyclopentadiene with molybdenum alkylidene 2 resulted in only the recovery of linear, soluble polymer. With the classical catalyst system 1, insoluble material was obtained, which was assumed to be crosslinked through olefin addition. These results disproved the idea that metathesis crosslinking can be induced by a critical chain length or concentration of polydicyclopentadiene. On the contrary, no indication of metathesis crosslinking was observed whatsoever for these polymerization systems.

CHAPTER 1
INTRODUCTION

Over the past 50 years, the field of polymer science has given chemists an opportunity to expand their scientific creativity through a new world of compounds which has become accessible. It is now possible to tailor-make new substances and materials with specific structures and properties, utilizing well-defined systems to obtain the desired product. Understanding the mechanisms responsible for the formation of these materials is integral to expanding the knowledge base which allows advances in technology. Although many polymerization methods are well understood, there are still some processes which are more difficult to examine, especially in the case of crosslinked polymers.

This dissertation seeks to provide insight into the polymerization of dicyclopentadiene, the only industrially important polymer made today via metathesis chemistry. For more than 25 years, the accepted mechanism for the formation of this crosslinked polymer has been one of exclusively ring-opening metathesis. Polymerization of the strained norbornene ring is assumed to occur first, followed by the subsequent metathesis of the cyclopentene unit, as depicted in Figure 1-1. This is a reasonable assumption, yet due to the difficulty associated with characterizing crosslinked polymers, it is nearly impossible to ascertain the mode of polymerization .

In order to help provide some understanding of what occurs during the polymerization of dicyclopentadiene, a model study was undertaken in which linear, soluble polymers were synthesized from compounds containing only one site of unsaturation. From these results, as well as from direct studies of the polymerization of

dicyclopentadiene and the reactivity of linear polydicyclopentadiene to metathesis, explanations can be made for the formation of the insoluble polymer.

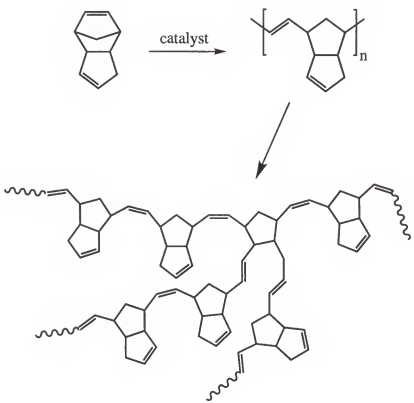


Figure 1-1. Presently accepted structure of crosslinked polydicyclopentadiene.

Due to the mechanistic questions raised in this study, a discussion of the metathesis reaction and catalyst systems is warranted. The field of ring-opening metathesis has received a vast amount of attention in the literature, and several excellent reviews are available.[1-4] This introductory chapter will serve to address the aspects of the metathesis reaction that are relevant to the research presented within this dissertation, including mechanistic aspects of metathesis, choice of catalyst systems, and an overview of the literature published on dicyclopentadiene polymerization.

History of the Metathesis Reaction

The olefin metathesis reaction, which has been studied for more than 40 years, continues to intrigue chemists with respect to the many new molecules which can be synthesized using this technique. The word metathesis originates from the Greek "meta" meaning change and "tithemi" meaning place. The term is applied in an organic chemical sense to describe the equilibrium interchange of two olefins by movement of bonding electrons to form two new olefins, as illustrated in Figure 1-2.

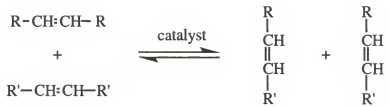


Figure 1-2. The olefin metathesis reaction.

The success of olefin metathesis as a synthetic tool can be attributed to outstanding advances in the fields of catalysis and organometallic chemistry. The reaction has prompted mechanistic investigations to explain how catalysts are able to accomplish this transformation at room temperature, and much is known today with respect to the nature of this chemistry. While metathesis is employed both in the synthesis of small molecules and in the preparation of polymers, this dissertation deals primarily with the utilization of olefin metathesis in polymerization chemistry.

With the inception of Ziegler-Natta polymerization in the 1950s, researchers in the field of polymer chemistry utilized the benefits of well-defined polymerization systems and organometallic chemistry for the advancement of polymer science. Metathesis polymerization was a natural outgrowth of Ziegler-Natta polymerization,

since both methods employ similar catalysts and alkylating agents. Compared with other polymerization techniques, including radical, anionic, cationic, and Ziegler-Natta, the area of metathesis polymerization is unique in that the olefin moiety is retained in the final polymer structure.

At DuPont in 1955, Anderson and Merckling[5] received a patent for the polymerization of norbornene with a Ziegler-Natta catalyst to afford a mixture of an oil and an infusible solid, which they did not characterize to determine the polymer structure. Although this might have been the first example of a metathesis polymer, it is Eleuterio[6] who must be credited with the discovery of metathesis polymerization based on a patent application filed in June 1957. This patent described the polymerization of several cyclic olefins, including cyclopentene and norbornene, with a molybdena or alumina catalyst that had been reduced with hydrogen and activated with lithium aluminum hydride. The unusual nature of the polymerization was discovered from ozonolysis of the norbornene polymer, which yielded only *cis*-cyclopentane-1,3-dicarboxylic acid, as shown in Figure 1-3. These findings were the first indication that metathesis polymerization results in a structure in which unsaturation is retained in the final polymer.

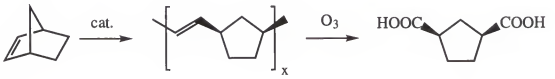


Figure 1-3. Ozonolysis of polynorbornene to yield only *cis*-cyclopentane-1,3-dicarboxylic acid.

In 1960, a paper was published in the open literature which showed that Ziegler-Natta catalysts could also form a polymer from norbornene which yielded *cis*-cyclopentane-1,3-dicarboxylic acid upon ozonolysis.[7] In this case, the proposed mechanism of the polymerization involved the cleavage of the σ bond adjacent to the

norbornene double bond, illustrated in Figure 1-4. It must have seemed at the time completely unreasonable to think that the cleavage of the double bond itself could be leading to polymer formation.

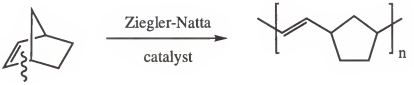


Figure 1-4. Early explanation of the mechanism for polymerization of norbornene with Ziegler-Natta catalysts.

It was still several more years before the generality of this reaction was first realized. In 1964, Banks and Bailey[8] published a paper that indicated that acyclic olefins undergo "disproportionation" reactions, involving the exchange of alkyl substituents between two olefins (see Figure 1-2). Even so, it was Calderon,[9-12] with the discovery that $WCl_6/EtAlCl_2/EtOH$ brought about rapid polymerization of cyclooctene and 1,5-cyclooctadiene, as well as the disproportionation of 2-pentene, who first realized that this disproportionation and the polymerizations were two aspects of the same equilibrium reaction. He termed the process "olefin metathesis," elegantly demonstrating that the double bonds are completely broken during the metathesis reaction of 2-butene with 2-butene-d_8 to yield only 2-butene-d_4, as shown in Figure 1-5.

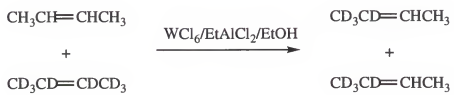


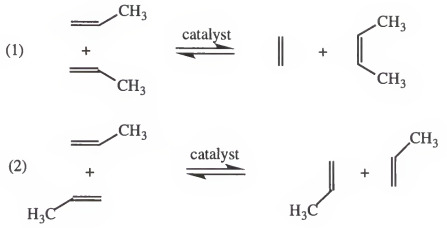
Figure 1-5. Metathesis exchange reaction of 2-butene with 2-butene-d_8 to yield only 2-butene-d_4.

The olefin metathesis reaction is useful in the synthesis of small organic molecules, as well as in the formation of specialty polymers. There are three broad classifications which fall under the heading of olefin metathesis, including exchange (A), polymerization (B), and ring closing metathesis (C), as illustrated in Figure 1-6. In general, these reactions are reversible, and are highly dependent on thermodynamic considerations in order for high conversions to be achieved. With the proper choice of catalyst, metathesis can proceed rapidly, with equilibrium being reached within a matter of seconds.[4]

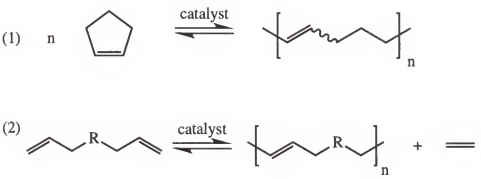
The first application of olefin metathesis to an industrial practice was done in 1966 by the Phillips Petroleum Company in their triolefin process,[4] which involved the synthesis ethylene and 2-butene from propene, as illustrated in Figure 1-6A. Although the equilibrium process had a maximum conversion in the range of 40%, any unreacted propene was recycled back to the reactor, minimizing waste. Both starting materials were inexpensive and readily available, creating the perfect conditions for a low cost plant which could operate with a capacity of 50,000 tons per year. Unfortunately, the plant was only in operation for six years, and was closed in 1972 after an increased demand for propene made this process impractical from an economic standpoint.

Two types of metathesis polymerizations have been defined to date, as illustrated in Figure 1-6B. Ring-opening metathesis polymerization (ROMP) is a chain polymerization process which generates high molecular weight polymers by exposing strained cyclic olefins to an appropriate catalyst. The reaction has precedence as far back as the 1950s, and is used commercially today to produce specialty polymers such as polynorbornene and polydicyclopentadiene. The ROMP reaction has long dominated the field of metathesis polymerization, and is discussed in greater detail later in this chapter.

A. Metathesis Exchange



B. Metathesis Polymerization



C. Ring Closing Metathesis

Figure 1-6. Examples of olefin metathesis reactions. A. Metathesis Exchange: (1) productive and (2) degenerate; B. Metathesis Polymerization: (1) ring-opening and (2) condensation; C. Ring Closing Metathesis.

Another approach to producing polymers with the same general type of repeat unit is also shown in Figure 1-6B. Acyclic diene metathesis (ADMET) is step polymerization chemistry which occurs by way of a condensation reaction to produce high molecular weight polymers. Opportunities in this area have begun to unfold over the past decade,[13-26] and it is now evident that the ADMET reaction joins ROMP polymerization as a viable method for generating high molecular weight molecules with well-defined structures.

Development of Mechanism

With the emergence of olefin metathesis polymerization, many studies were directed at better understanding the mechanism that leads to the formation of unsaturated polymers. The first significant pieces of information to assist in the development of a formal mechanism were the results of Calderon.[12] His study of metathesis exchange between 2-butene and 2-butene-d_8 to yield only 2-butene-d_4, as shown in Figure 1-5, proved very important, since it established that the double bond was completely broken during the reaction.

Although it is relatively straightforward to prove complete breaking of the double bond for the metathesis of small molecules, it is slightly more difficult to demonstrate carbon-carbon double bond severage during polymerization. However, Dall'Asta and Montroni[27] elegantly demonstrated double bond cleavage through the copolymerization of 1-^{14}C-1-cyclopentene and cyclooctene. After ozonolysis of the copolymer and isolation of the products as α,ω-diols, the mixture was characterized for ^{14}C activity. As illustrated in Figure 1-7, all of the ^{14}C was found in the C_5 fraction, indicating cleavage of the double bond. Any other type of reaction would have resulted in ^{14}C incorporation into the C_8 portion of the polymer chain.

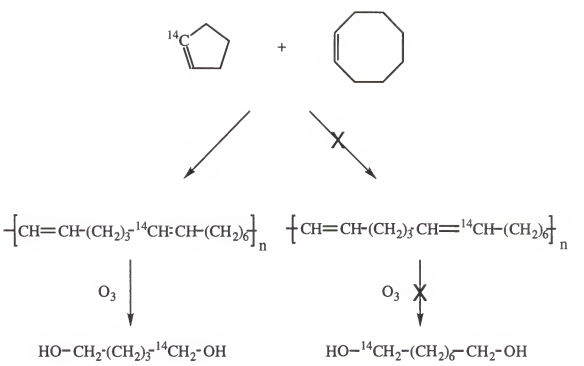


Figure 1-7. Evidence for breaking of C-C double bond during ring-opening metathesis polymerization.

From these studies with atom labeling, it could be reasonably assumed that the carbon-carbon double bond was completely broken during the olefin metathesis reaction. It could also be inferred that the same mechanism was responsible for olefin exchange as well as metathesis polymerization. Still, it was nearly ten years after these discoveries before the metathesis community could agree on a feasible mechanism for the metathesis reaction.

Pairwise Mechanism

The first general mechanism for olefin metathesis, proposed by Bradshaw[28] in 1967, involved the formation of a 'quasi-cyclobutane' complex. This pairwise mechanism worked through the interaction of the transition metal orbitals with the π orbitals of the

olefin to generate a 'quasi-cyclobutane', which then exchanged groups to yield two new olefins, as given in Figure 1-8. Much additional work was conducted in this area for several years, during which time the structure of the 'quasi-cyclobutane' and the mechanism by which it formed were debated.

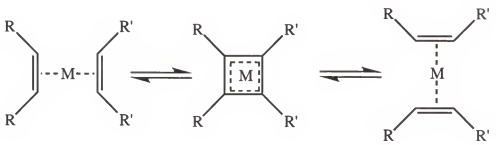


Figure 1-8. Pairwise 'quasi-cyclobutane' mechanism for olefin metathesis, where M = transition metal catalyst and ligands.

Several different mechanisms can be proposed to describe the pairwise exchange of fragments between olefins, and experiments were conducted to test these possibilities. As the various studies were carried out, two interesting results cast shadows of doubt on the viability of the pairwise mechanism. The first involved the cross metathesis of cyclopentene and 2-pentene, as illustrated in Figure 1-9. If the pairwise mechanism were operating, only product B would be formed. However, Chauvin[29] found that products A, B, and C were formed in the predicted statistical array. These results lead to the proposal of another mechanism, based on a carbene intermediate, which will be discussed in the next section.

The other main contradiction of the pairwise mechanism came from the field of polymer chemistry and the results of ring-opening metathesis polymerization. If the pairwise mechanism were operating, the molecular weight of the polymer would increase in a stepwise fashion, and gradually increase as the reaction proceeded through the

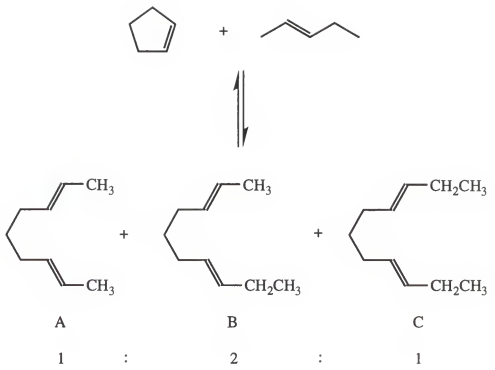


Figure 1-9. Products from cross metathesis of cyclopentene and 2-pentene.

formation of large macrocycles. However, it was observed that the molecular weight distribution during the initial stages of the reaction is near to that of the final reaction mixture,[30] which is consistent with a chain process. Although these experiments suggested that the 'quasi-cyclobutane' mechanism was inaccurate, the mechanism was still generally accepted and applied for nearly a decade.

Non-Pairwise Mechanism

An alternative to the 'quasi-cyclobutane' mechanism, the carbene mechanism proposed by Herrison and Chauvin[29] in 1970 is derived from the results obtained from the cross metathesis of cyclopentene and 2-pentene (see Figure 1-9). This mechanism

involved two key steps: 1) the initial formation of a metal alkylidene (or carbene), and 2) propagation of the reaction through a metallacyclobutane intermediate, leading to olefin-alkylidene exchange. Figure 1-10 illustrates the carbene mechanism, which is the currently accepted view on how metathesis chemistry transpires. The reacting olefin coordinates to the metal carbene, then undergoes an insertion to yield a metallacyclobutane. Productive cleavage of this metallacycle generates a new reactive alkylidene.

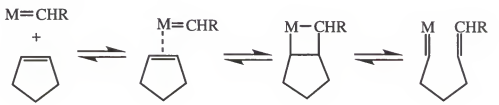


Figure 1-10. Metal carbene mechanism proposed by Herrison and Chauvin.[29]

As described earlier in Figure 1-9, the cross metathesis of a cycloolefin with a non-symmetric olefin yields three products in the predicted statistical ratios, a result that is in agreement with the metal carbene mechanism. Also, as mentioned previously, the metal carbene mechanism gives a good explanation of the molecular weight distributions found in the polymerization of cyclic olefins. As demonstrated for the polymerization of cyclopentene (Figure 1-10), the metal carbene mechanism justifies the chain growth of the polymer to yield high molecular weights, even in the initial stages of the reaction.

Although these two results are not enough in themselves to unequivocally prove the carbene mechanism is operating, more supporting evidence has been derived from the field of organometallic chemistry. A number of isolable carbene complexes have been shown to be active catalysts for ring-opening metathesis polymerization, even without added Lewis acids or alkylating agents. Katz and coworkers[31] demonstrated that

Casey's[32] diphenyl tungsten carbene complex, $(CO)_5W{=}CPh_2$, could be used as a catalyst for the ring-opening metathesis polymerization of various cycloolefins, and there was even some evidence that the diphenylmethyl moiety was incorporated into the polymer (Figure 1-11). Although the rates of polymerization with this catalyst were slow in comparison with Calderon's $WCl_6/EtAlCl_2/EtOH$ catalyst system, high molecular weights were obtained and the reactions were found to be highly stereospecific.

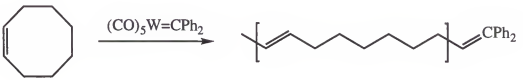


Figure 1-11. Polymerization of cyclooctene with Casey's tungsten complex.

Even with all of the evidence that supports the metal carbene mechanism, it has taken more than two decades for the metathesis community to accept this mechanism as the one that leads to olefin metathesis. Much of the credit for proving this mechanism goes to researchers in the field of organometallic chemistry, who are responsible for conducting experiments dealing with metal carbene complexes and their activity toward olefin metathesis. The importance of organometallic chemistry in the development of olefin metathesis catalysts is discussed in the following section.

Catalyst Systems

The number of catalyst systems capable of initiating metathesis reactions is truly overwhelming. There are a few single compound catalysts, and literally thousands of multiple component catalyst systems. Metathesis catalysts can be heterogeneous (or supported) as well as homogeneous, although the distinction between the two is often

blurred. Regardless of the physical state of the catalyst, the species responsible for achieving the metathesis reaction has been determined to be a transition metal-carbon double bond, or metal alkylidene (carbene).

In general, catalyst systems fall into two categories, which are classified as classical catalysts and preformed alkylidenes. By far, the classical catalyst systems find more utility in industrial processes due to their tolerance to impurities and relatively inexpensive cost of use. However, with recent advances in the field of well-defined preformed alkylidenes, this area could also see additional application in industrial processes. The advantages and shortcomings of both types of catalyst systems will be discussed in the following sections.

Classical Catalyst Systems

Classical metathesis catalysts, as shown in Table 1-1, are typically composed of a transition metal halide and a non-transition metal cocatalyst which form a metathesis active alkylidene *in situ*. Of the available transition metals, the most active for olefin metathesis are molybdenum, tungsten, tantalum, and rhenium, with tungsten and molybdenum being used most often. There are also some catalyst systems which make use of titanium, ruthenium, osmium and iridium to polymerize highly strained cyclic olefins, although these are less effective for acyclic or very stable cyclic olefins.

Classical catalysts tend to be ill-defined, due to the unknown nature of the true active catalyst, and the presence of a Lewis acid cocatalyst in the system which can lead to side reactions that compete with metathesis polymerization. Although the occurrence of side reactions is often a drawback, classical catalysts find favor in industrial processes as they are relatively inexpensive to use.

Table 1-1. Representative classical catalyst systems for metathesis polymerization.

Catalyst complex	Solvent/Temp (°C)
$MoCl_2(NO)_2(PPh_3)_2$/ $Me_2Al_2Cl_3$	Chlorobenzene, 25°[33,34]
$Bu_4N[Mo(CO)_5COPh$/ $MeAlCl_2$	Chlorobenzene, 20°[35]
(py)$Mo(CO)_5$/ $EtAlCl_2$/NBu_4Cl	Chlorobenzene, 20°[36,37]
(tol)$W(CO)_3$	Heptane, 98°[38]
WCl_4/BuLi	Benzene, 20°[39]
$PhWCl_3/AlCl_3$	Chlorobenzene, 20°[39]
$ReCl(CO)_5/EtAlCl_2$	Chlorobenzene, 90°[40]

Classical catalysts can be employed quite successfully in the production of polymers through ring-opening metathesis polymerization (ROMP). Although the use of classical catalysts is often accompanied by various side reactions, ROMP reactions are quite forgiving in terms of catalyst selection since they are based on chain polymerization principles. In chain addition polymerizations, high molecular weight polymers are formed early in the reaction, and the extent of polymerization through the desired mechanism usually outweighs the extent of side reactions. Any side reactions that occur during ROMP polymerization usually occur at a rate slower than metathesis, and would generate short oligomers that are removed with precipitation and purification of the polymer.

By comparison, reactions of acyclic olefins with metathesis catalysts occur in a step-wise fashion. The strict requirements of step growth polymerization chemistry for

purity and stoichiometric balance demand precise catalyst structures in order for the polymerization of acyclic dienes to proceed to the formation of high molecular weight polymers. For this reason, early efforts at condensation of acyclic dienes with classical catalysts systems were met with only limited success.[34,41,42]

Preformed Alkylidenes

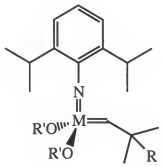
Although olefin metathesis aided by the utilization of classical catalyst systems has been carried out for some time, the advent of well-defined catalysts is a rather recent development. Stable metal carbenes were first synthesized by Fischer,[43] and hundreds are now known. These carbenes fall into two separate categories, as illustrated in Figure 1-12. The first group consists of Fischer-type carbenes, compounds in which the metal carbene carbon acts in an electrophilic manner (a).[43] Fischer-type carbenes are low valent compounds which are typified by the presence of a heteroatom, such as O, N, or S, bonded to the carbene carbon. Since these are 18 electron complexes which are coordinatively and electronically saturated, Fischer carbenes are not usually active catalysts for olefin metathesis. However, with the addition of a cocatalyst or by activation photochemically or by heating, a coordination site can be formed to yield a metathesis active compound.[4]

(a) (b)

Figure 1-12. Examples of (a) electrophilic[43] and (b) nucleophilic metal carbenes.[44,45]

Most of the recent research that has been conducted in the field of olefin metathesis has been based on using well-defined Schrock-type carbenes. By comparison

to the Fischer-type carbenes, Schrock alkylidenes are usually formed from high oxidation state metals, do not have a heteroatom bonded to the carbene carbon, and are usually characterized as having a nucleophilic carbene carbon, as shown in Figure 1-12b. The best known alkylidenes for olefin metathesis are of the form $M(NAr)(CHC(CH_3)_2R)(OR')_2$, where M = W[46] or Mo,[47] and are illustrated in Figure 1-13.



M = W, Mo

R = -CH_3, -Ph

R' = -*i*-Bu, -$CCH_3(CF_3)_2$

Figure 1-13. Schrock's alkylidene for olefin metathesis.

Since they do not require a Lewis acid cocatalyst in order to be metathesis active, Schrock alkylidenes are known for exclusively catalyzing metathesis chemistry, without the competing side reactions associated with classical systems The effect of an acid cocatalyst on the reaction mechanism has been illustrated by Wagener and coworkers[48] in a model compound study which distinguished between competing mechanistic pathways, as depicted in Figure 1-14. The model reagent, styrene, could have either produced stilbene through metathesis chemistry, or could have undergone vinyl addition polymerization to yield polystyrene. The results of this study show that only polystyrene was generated in the presence of the classical catalyst system (WCl_6/$EtAlCl_2$). However, the mechanistic alternative is realized with a well-defined preformed alkylidene. Utilizing Schrock's hexafluoro tungsten alkylidene resulted in exclusively clean

metathesis chemistry, producing only stilbene in quantitative yields. This observation demonstrated that a catalyst system not possessing a Lewis acid cocatalyst must be chosen in order to avoid competing vinyl addition chemistry.

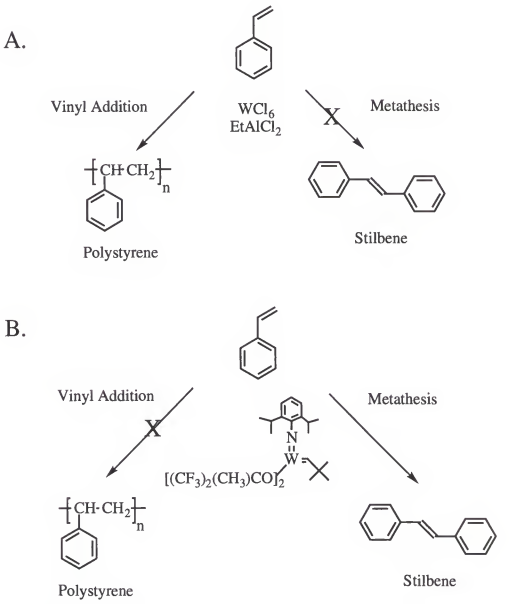
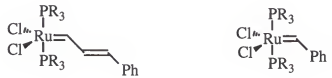


Figure 1-14. Comparison of metathesis activity for classical $WCl_6/EtAlCl_2$ catalyst system (A) and Schrock tungsten alkylidene (B).

Recently, other catalyst systems have been shown to be effective in producing high molecular weight metathesis polymers. For example, the class of ruthenium alkylidenes reported by Grubbs,[49-51] as illustrated in Figure 1-15, are useful in both ring-opening metathesis polymerization and metathesis exchange reactions of acyclic compounds. One advantage of these catalytic initiators that distinguishes them from Schrock-type systems is that they are more tolerant of polymerization conditions. For example, these ruthenium alkylidenes can be used successfully in the presence of water and other protic solvents.[49] Consequently, the usual time intensive purification of monomers and exclusion of atmospheric impurities are obviated, allowing metathesis chemistry to become a benchtop procedure.



R = cyclohexyl or phenyl

Figure 1-15. Grubbs ruthenium based alkylidenes for olefin metathesis.

The proper choice of catalyst is essential for the realization of metathesis polymerization chemistry. For processes such as ring-opening metathesis polymerization, where reaction conditions are not extremely sensitive to impurities, a classical catalyst system can be employed with great success. However, in experiments where a well-defined catalyst with an exact structure is needed to ensure a known polymerization mechanism, a preformed alkylidene which does not require a Lewis acid cocatalyst must be employed.

Ring-Opening Metathesis Polymerization

Research in the area of ring-opening metathesis polymerization (ROMP) was instrumental in determining the mechanism by which olefin metathesis occurs. The polymerization of cycloolefins was found to occur in a chain-wise manner, yielding molecular weight distributions during the initial stages of the reaction near to that of the final reaction mixture.[30] These results help to corroborate other facts that support the metal carbene mechanism. Over the past three decades, ring-opening metathesis polymerization has been studied extensively, and continues to be the most studied metathesis polymerization technique in industrial and academic research.

The polymerization occurs by a chain growth mechanism to produce linear, high molecular weight polymers, as depicted in Figure 1-16 for the polymerization of cyclopentene. The first stage of the polymerization cycle involves the coordination of an olefin to the metal carbene complex (A). The monomer then undergoes an insertion reaction to form a metallacyclobutane intermediate (B). The metallacycle subsequently breaks down to form a new π complex (C), and finally completely dissociates to form a new propagating alkylidene (D). Fresh monomer can then coordinate with this species, and chain propagation continues until all available monomer is consumed.

Thermodynamic Aspects

As implied from Figure 1-16, ring-opening metathesis polymerization, like all ring-opening polymerizations, is an equilibrium process which is governed by both kinetic and thermodynamic factors. The considerations involved in polymerization of cyclic olefins are complex and interrelated, working together to make ring-opening metathesis polymerization feasible. The single most important factor in determining the

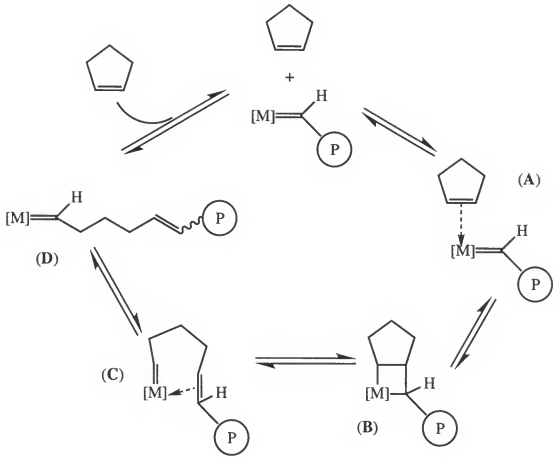
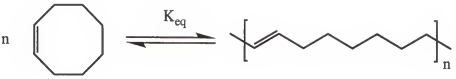


Figure 1-16. Ring-opening metathesis mechanism as applied to cyclopentene. [M] = catalyst complex and P = growing polymer chain.

ease of polymerization of a cycloolefin is the thermodynamic stability of the monomer with respect to the linear polymer structure.[52] As shown in Equation 1-1, this equilibrium polymerization is described by the equilibrium constant, K_{eq}, which indicates the amount of monomer present in the system relative to polymer concentration (Equation 1-2). Cyclic oligomers are present in the polymerization mixture as well, although they usually occur in small amounts and are often ignored when discussing the thermodynamics of polymerization.

The equilibrium between monomer and polymer is also described by the Gibbs free energy equation (1-3). In order for the reaction to proceed to the formation of

polymer, the value of ΔG must be negative. The release of ring strain on conversion of



(1-1)

$$K_{eq} = [\text{polymer}] / [\text{monomer}] \qquad (1\text{-}2)$$

monomer to polymer is expressed by the enthalpy term, ΔH. If the ring-opened polymer is more thermodynamically stable than the cyclic monomer, this ΔH term is negative, indicating an exothermic reaction. As with most polymerization processes, the entropy (ΔS) of the system decreases as polymerization occurs, thus having an unfavorable effect on the free energy (ΔG). It is well known that ring-opening polymerizations of all types occur readily for 3-, 4-, 8-, and larger-membered rings, since the linear ring-opened polymer is thermodynamically more stable than the cyclic monomer. In general, monomers with greater ring strain (larger negative value for ΔH of reaction) are more reactive for ring-opening polymerizations.

$$\Delta G = - RT \ln K_{eq} = \Delta H - T\Delta S \qquad (1\text{-}3)$$

The changes in enthalpy and entropy for the ring-opening metathesis polymerization of several cycloolefins have been calculated, as well as experimentally determined, and are summarized in Table 1-2.[4] In order for polymerization to occur, the ΔG term for the reaction must be negative. Notable is the case of cyclohexene, for which polymerization is not favorable at room temperature due to the failure of the small amount of ring strain present in the monomer ($\Delta H \approx 0$) to overcome the $-T\Delta S$ term. However, for each possible monomer concentration, there exists a ceiling temperature

(T_c), where the rates of polymerization and depolymerization are equal, generating a free energy value of $\Delta G = 0$. Below the ceiling temperature, the polymerization is made feasible by reducing the contribution of the entropy term to the Gibbs free energy equation. When the concentrations of cyclohexene are made to be very high, and the reaction temperatures are quite low (less than -23°C), oligomers can be obtained.[53,54]

Table 1-2. Thermodynamic parameters for the formation of solid polymers from ROMP of various liquid cycloolefins at 25°C.[4]

Monomer	Polymer	ΔH (kJ/mol)	ΔS (J/°K mol)	ΔG (kJ/mol)
cyclobutene	cis	-121	-52	-105
cyclopentene	cis	-15.4	-51.8	-0.3
	trans	-18	-52	-2.6
cyclohexene	cis	2	-31	+6.2
	trans	-2	-28	+7.2
cycloheptene	70% trans	-18	-37	-7
cyclooctene	48% trans	-13	-9	-13
norbornene	45% trans	-62.2	-50	-47

Monomer concentration is also very important in ring-opening metathesis polymerization, especially for systems where ΔG is only slightly negative. For example, in the polymerization of cyclopentene, $\Delta G = -0.3$ for the formation of *cis* polymer, and $\Delta G = -2.6$ for the *trans* polymer. By simply adjusting the concentration of monomer in the system, the equilibrium can be shifted towards polymer or back to monomer. Schrock[55] demonstrated that the polymerization of cyclopentene with the alkylidene $W(CHC(CH_3)_2Ph)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{Pr}_2)(OCCH_3(CF_3)_2)_2$ can be entirely reversed by applying vacuum to the system, effectively stripping away the monomer units from the living polymer chain (Figure 1-17).

In addition to the size of the ring, substituents on the ring play an important part in determining the polymerizability of cycloalkenes. Generally, substituents on a

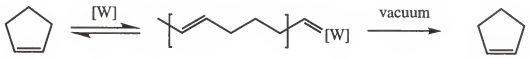


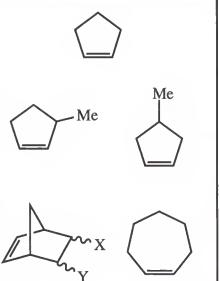
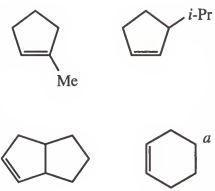
Figure 1-17. Living polymerization of cyclopentene and subsequent reversal of reaction by application of vacuum. [W] = $W(CHC(CH_3)_2Ph)(N\text{-}2,6\text{-}C_6H_3\text{-}iPr_2)(OCCH_3(CF_3)_2)_2$.

cycloolefin have an unfavorable effect on ΔG for ring-opening polymerization of any kind, by decreasing the enthalpy change (ΔH) for the reaction. This result often arises from steric strain differences between the monomer and the polymer.[52] The substituted cycloolefin is usually more thermodynamically stable than its ring-opened counterpart. Substituents on a cycloolefin have less of an effect on the entropic changes that occur during the reaction, since ΔS of polymerization comes primarily from loss of translational entropy of the monomer.[52] Vibrational and rotational energy losses in the monomer are essentially balanced by gains in the polymer vibrational and rotational energies.

Table 1-3 illustrates a few examples of compounds that are and are not polymerizable by ring-opening metathesis. The compounds listed as not polymerizable can be assumed not to undergo ROMP to form high polymer because ΔG is positive for these compounds under all conditions that have been investigated.[4] These compounds which are reported not to polymerize under standard metathesis conditions could simply have been examined above their respective ceiling temperatures. Perhaps detailed studies of ceiling temperatures for these compounds would determine if polymer is formed at lower temperatures.

The issue of polymerizability for five-membered rings is a challenging metathesis question. Cyclopentene is polymerizable, as noted in Table 1-3, although the extent of polymerization is highly dependent on monomer concentration and reaction temperature. Some cyclopentenes with methyl substituents are also polymerizable if the methyl group is positioned appropriately. Both 3-methyl- and 4-methylcyclopentene will polymerize with typical metathesis catalysts at room temperature, yet 1-methylcyclopentene will not react. Additionally, when the bulk of the alkyl substituent is increased, as in the case if 3-isopropylcyclopentene, polymerization does not ensue. Disubstituted cyclopentenes have also been shown to be non-reactive towards olefin metathesis chemistry,[4] a result which is integral to the work presented in this dissertation.

Table 1-3. Polymerizability of various cycloolefins by ring-opening metathesis.[4]

Polymerizable	Not Polymerizable
	

[a] Cyclohexene has been shown to generate a small amount of oligomer when exposed to a metathesis catalyst below -23°C.[53,54]

There is little doubt that release of ring strain pushes the equilibrium for ROMP in favor of polymer formation; however, Patton and McCarthy[56] have suggested that this is not what causes highly strained rings to polymerize faster than their less strained counterparts. In a study of the rates of polymerization of norbornene versus cyclooctene with WCl_6/Me_4Sn, they found that the rate of polymerization of norbornene was too high to measure, but was estimated at >100 times faster than cyclooctene. When norbornene was added to an ongoing polymerization of cyclooctene, the rate of disappearance of cyclooctene increased until all of the norbornene was consumed, then the rate returned to its original value. These results were interpreted as a consequence of the activity of the growing metal carbene rather than just a function of ring strain. The alkylidene formed from addition of cyclooctene is deactivated through the formation of an olefin-metal complex (Figure 1-18), whereas the alkylidene generated from norbornene is more rigid, thereby preventing complexation.

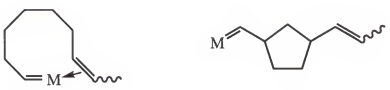


Figure 1-18. Representation of alkylidenes generated from cyclooctene and norbornene.

The discussion in this section emphasizes that thermodynamic factors play an integral role in determining the viability of the metathesis reaction. Release of ring strain from a monomer and the thermodynamic stability of the polymer over that of the monomer are the major contributors to the ease of ring-opening metathesis. In general, ideal reaction conditions for ROMP are high monomer concentration and low temperature, as well as the utilization of highly strained monomers.

Bicyclic Systems

Due to the amount of ring strain present in bicyclic monomers, as well as the relative rigidity of the metal alkylidene formed upon metathesis exchange, these systems are ideally suited to ring-opening metathesis polymerization. By far, this class of compounds has been the most studied, which can be attributed in part to the vast number of derivatives of norbornene which have been synthesized and polymerized.[4] Bicyclic compounds such as norbornene and dicyclopentadiene are excellent candidates for examining ROMP, and are in fact utilized industrially to make specialty materials. There are many other types of bicyclic compounds which undergo ring-opening metathesis polymerization, generating polymer structures that are both unique and fascinating.

As touched on in the previous section, ring strain is often the driving force for metathesis polymerization. Compounds with fused cyclobutene and cyclopentene rings are often polymerized using typical metathesis catalysts. In the case of fused cyclobutenes, the olefin in the C_4 ring undergoes metathesis rapidly to form ring-opened polymers. Figure 1-19 gives a few examples of interesting fused cyclobutene systems, and their respective polymers. Some of these polymers (see Figure 1-19c,d) undergo further reaction at higher temperatures to generate polyacetylene through a retro-Diels-Alder reaction.

Contrary to the case of fused cyclobutenes, the reactivity of monomers containing a fused cyclopentene (those which are not norbornene derivatives) towards ring-opening metathesis is more varied. Figure 1-20 illustrates a few examples of this class of monomer. As is the case with the first two compounds (Figure 1-20a,b), there is not enough ring stain released when the monomer reacts to outweigh the unfavorable entropy loss of the polymerization, so the reaction does not proceed. These compounds are important for discussion in this dissertation, as both structures are present during the

polymerization of dicyclopentadiene, and will be considered in detail in Chapter 3. As noted for the reactions given in Figure 1-20c,d, these monomers are considerably more strained, and undergo facile ring-opening metathesis polymerization.

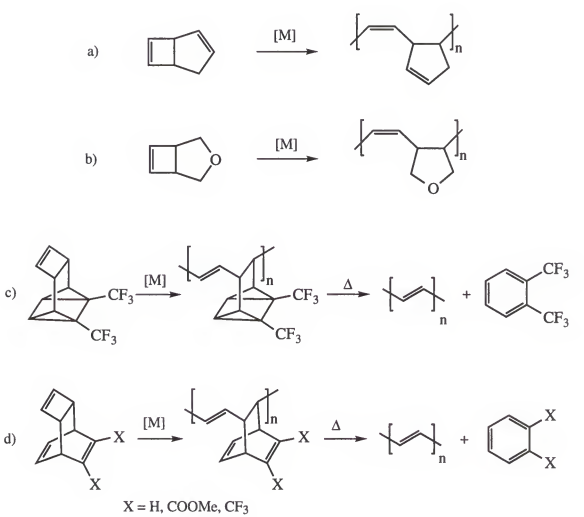


Figure 1-19. Ring-opening metathesis polymerization of several C_4 bicyclic systems. a) bicyclo[3.2.0]hepta-2,5-diene,[57] b) 6-oxo-bicyclo-[3.2.0]hept-2-ene,[58] c) 7,8-bis(trifluoromethyl)tricyclo-[4.2.2.$0^{2,5}$.$0^{7,10}$.$0^{8,9}$]dec-3-ene,[59] d) tricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene, 7,8- derivatives. H,[60,61] COOMe,[61,62] CF_3.[60,61,63,64]

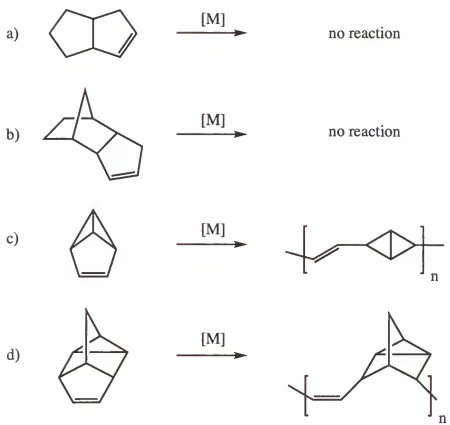


Figure 1-20. Reactivity of various fused cyclopentene rings toward ROMP. a) bicyclo[3.3.0]oct-2-ene,[65] b) tricyclo[5.2.1.$0^{2,6}$]dec-3-ene,[65] c) benzvalene,[66,67] and d) deltacyclene.[68]

Also included with the various fused cyclopentene compounds which have been studied for their reactivity toward ROMP are norbornene (or bicyclo[2.2.1]hept-2-ene) and its derivatives, which number in the hundreds and will not be discussed here. There are several excellent reviews of metathesis[1,2,4] which detail work in this area, and should be consulted if additional information is desired. Norbornene has received a considerable amount of attention, as it is an inexpensive monomer which can be polymerized using virtually any metathesis catalyst. The polymerization of norbornene was first described in the literature by Truett in 1960,[7] and since then has been applied to living ROMP, the synthesis of various block copolymers, and even to generating star-shaped polymers.[4]

The growing polymer chain can be terminated by the addition of a ketone such as benzophenone[69] or aldehyde such as terephthaldehyde[70] to form a C=C through a Wittig-type reaction (Figure 1-21). If these ketones and aldehydes are substituted,[71] these sites can be employed to construct a diverse group of tailor-made functionalized polymers.

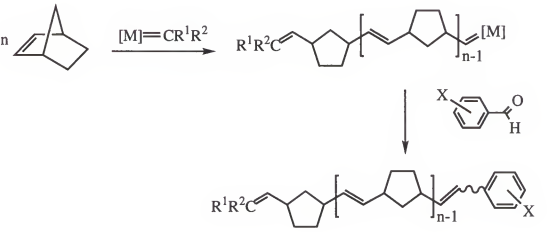


Figure 1-21. Polymerization of norbornene with metathesis catalyst ([M] = metal and ligands) followed by end-capping with functionalized benzaldehyde. X = CF_3, OMe, NMe_2, CN, NO_2, CHO, CO_2Me, NH_2, Cl.

The discussion thus far in this section has centered around cycloolefins with one (reactive) site of unsaturation, so all of the polymers resulting from these compounds have been linear in nature. However, bicyclic monomers with two olefins are well known, and under appropriate conditions, are reactive to form crosslinked network polymers. Among these, dicyclopentadiene has received the most attention due to its application in industrial chemistry as an inexpensive, readily available monomer. The mechanisms responsible for the formation of polydicyclopentadiene are the focus of this dissertation; therefore, a discussion of the history of dicyclopentadiene polymerization is warranted.

Polymerization of Dicyclopentadiene

The polymerization of dicyclopentadiene has been known since the late 1960's, and polydicyclopentadiene remains the most important polymers used industrially that is synthesized from ring-opening metathesis polymerization. The monomer is a by-product from petroleum distillation, and finds utility due to its abundance and low cost. The polymer which results from polymerization with classical Lewis acid cocatalyst systems is quite hard and tough, making it an ideal material for uses such as automobile bumpers, as well as in golf cart and snowmobile bodies.

The first catalyst systems studied for their effectiveness in ROMP of dicyclopentadiene were classical systems of $MoCl_5/Et_3Al$[72] and WCl_6/Et_2AlCl.[73] Since these initial studies, many other catalyst systems have been examined, including ones based on titanocyclobutanes,[70,74,75] $TiCl_4$,[76] $ReCl_3$,[77] $ReCl_5$,[77,78] and many $WCl_n(OR)_{6-n}$ compounds,[79-83] to mention the most common. Over the past decade or so, polydicyclopentadiene has found application as an industrially synthesized polymer made by reaction injection molding (RIM) techniques. The two component catalyst systems typically used for ring-opening metathesis polymerization are perfectly suited to a RIM process.

In the reaction injection molding process (Figure 1-22), two separate streams of reactants are combined at the mixhead and injected into a preheated mold. Each stream contains monomer and one component of the catalyst system, along with elastomers, fillers, and reaction moderators.[1] The elastomers help to increase the viscosity of dicyclopentadiene to afford better mixing, while the reaction moderators, usually Lewis bases, serve to control the initiation of the reaction, delaying polymerization until the components are well mixed and have traveled into the mold.

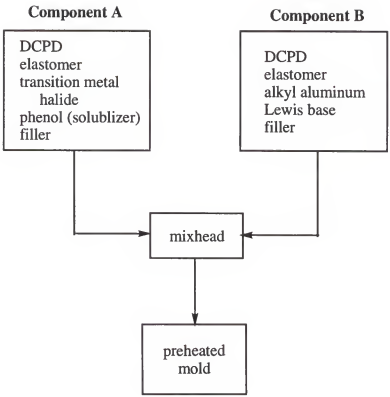


Figure 1-22. Representative scheme for reaction injection molding (RIM) of dicyclopentadiene.

During the polymerization of dicyclopentadiene with metathesis catalysts, a large amount of heat is generated from the opening of the strained norbornene ring, as illustrated by the thermal profile given in Figure 1-23.[84] Within a few seconds of being deposited in the preheated mold, the mixture reaches a gel point, then the temperature quickly rises to an exotherm maximum of over 200 °C. This increase in temperature is due exclusively to the heat that is released during the ROMP reaction - no outside heat source is acting on this system.

When classical catalyst systems containing a Lewis acid cocatalyst are employed for the ROMP of dicyclopentadiene, the resulting polymer is usually only slightly soluble in organic solvents, indicating that a crosslinked product has formed. It is thought that

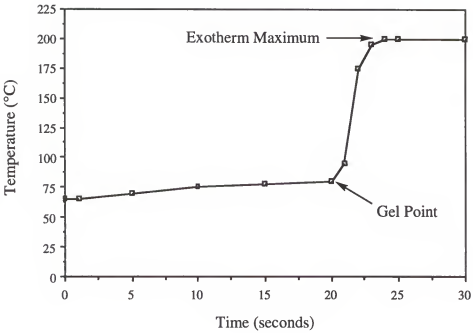


Figure 1-23. Thermal profile for a typical RIM polymerization of dicyclopentadiene with inhibitor.[84]

the polymerization occurs in two stages, with initial formation of linear polymer, followed by a secondary metathesis reaction of the pendant cyclopentene to yield a crosslinked thermoset polymer (Figure 1-24), with predominantly *cis* double bond geometry, depending on catalyst choice. Although these reactions are shown to be consecutive, there is some evidence that the olefin in the cyclopentene begins to react before all of the strained norbornene-type double bonds are consumed.[1]

The nature of the material formed during the polymerization of dicyclopentadiene, including double bond geometry and crosslink density, is ultimately determined by the catalyst systems which are utilized. Many catalyst systems have been studied for their reactivity in the polymerization of dicyclopentadiene, and it seems that the formation of a

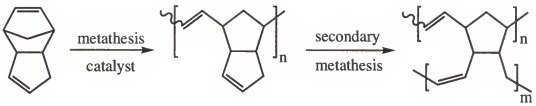


Figure 1-24. Generally accepted two-stage mechanism for the polymerization and crosslinking of dicyclopentadiene with metathesis catalysts.

linear, soluble polymer is highly dependent upon the choice of transition metal halide, as well as on the Lewis acidity of the cocatalyst. Table 1-4 summarizes several catalyst systems that have been employed, where the polymers ranged from completely soluble to completely insoluble. In general, the more active the transition metal is towards metathesis, and the more Lewis acidic the cocatalyst, the more likely it is that the catalyst will form an insoluble polymer.[78]

Table 1-4. Influence of transition metal and cocatalyst on soluble fraction of polymer formed from dicyclopentadiene.[78]

Catalyst	Polymer Yield (%)	% Soluble Polymer
$MoCl_5$	10	5
$OsCl_3$	15	5
WCl_6	10	10
$ReCl_5$	13	90
$ReCl_5/Et_2AlCl$	100	0
$ReCl_5/EtAlCl_2$	100	0
$ReCl_5/Me_4Sn$	80	100

In addition to the amount of insoluble polymer formed, the nature of the repeat units occurring in a sample of polydicyclopentadiene are also dependent on the catalyst system. Dall'Asta and coworkers[73] studied the homopolymerization of dicyclopentadiene with several Ziegler-Natta catalysts and found that six different repeat units, as shown in Figure 1-25, could be assigned on the basis of infrared spectroscopy. Quite remarkable differences are found for the various catalyst systems, as can be seen from the summary for selected catalysts in Table 1-5. With most of the catalytic systems that were investigated, the majority of the polymer that was formed was insoluble, so all data regarding repeat units was reported only for the soluble polymer fractions. Only one of the several catalysts studied by Dall'Asta and coworkers, $MoCl_5/AlEt_3$ in heptane at -20 °C, afforded a sample in which evidence for the ring-opening metathesis of the fused cyclopentene was observed, although the yield for this

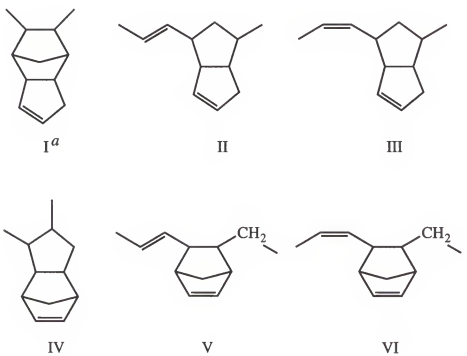


Figure 1-25. Possible repeat units found in the polymerization of dicyclopentadiene. [a]Can occur as *endo* or *exo*.[73]

Table 1-5. Distribution of monomer repeat units in polydicyclopentadiene with various catalyst systems.[73]

Catalyst Composition	Temp. (°C)	Polymer Yield (%)	Structure of repeat unit (in %)					
			I[a]	II	III	IV	V	VI
$TiCl_4$	-20	3	100	trace	0	trace	0	0
$MoCl_5/AlEt_3$	-20	1	0	20	20	30	15	15
WCl_6	-20	77	85	trace	0	15	0	0
WCl_6/Et_2AlCl	-80	42	0	50	50	0	0	0
WCl_6/Et_2AlCl	-20	13	0	15	85	0	0	0

[a] *endo* and *exo* forms.

system was trivial. This result is significant, since the accepted mode of crosslink formation in the polymerization of dicyclopentadiene by classical catalysts is assumed to be metathesis of this pendent ring. With typical industrial catalyst systems of WCl_6 with alkyl aluminum compounds, metathesis of this ring was never observed; however, olefin addition of the cyclopentene double bond was detected.

A recent study of the polymerization of dicyclopentadiene was conducted by Fisher and Grubbs[75] utilizing well-defined catalysts. The formation of insoluble polydicyclopentadiene from these systems was attributed to the equilibrium metathesis polymerization of the pendant cyclopentene at high monomer concentrations. Questions arise about the feasibility of this explanation, since this would involve the metathesis of a disubstituted cyclopentene to form crosslinks, which is thermodynamically much less favorable than the metathesis ring-opening of the norbornene unit. Fisher and Grubbs presented evidence that a critical monomer concentration is necessary for crosslinking to occur. In solution, where the concentration of dicyclopentadiene is kept below 1.0 M, the polymer remains completely soluble when initiated with Schrock's tungsten and

molybdenum alkylidenes (see Figure 1-13 for structures) at 70 °C. However, when neat monomer was polymerized (~ 7 M), the resulting mixture consisted of approximately 50% insoluble material, 25% soluble polymer, and 25% unreacted monomer. Additional evidence has also been presented that this crosslinking reaction is reversible, which is similar to what is observed for the polymerization of cyclopentene.[75]

Although these studies of the polymerization of dicyclopentadiene present some support for a metathesis crosslinking mechanism, there is no definitive way to determine how crosslinks are formed in an insoluble polymer. The research presented in this dissertation was undertaken for this reason. By closely examining the reactivity of the olefins present in dicyclopentadiene, more information about the mechanisms which are responsible for polymerization could be obtained. A better understanding of these mechanisms could potentially prove to be valuable to industrial chemists who rely on generating specific materials with distinct properties. Additionally, this information holds great academic value, since assumptions about structures of the crosslinked polydicyclopentadiene network have been made for nearly 25 years.

CHAPTER 2

EXPERIMENTAL

Instrumentation and Analysis

^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) were recorded on a Gemini-Series NMR Superconducting Spectrometer system. All NMR spectra were taken in chloroform-*d* ($CDCl_3$) or toluene-d_8 (C_7D_8) unless otherwise noted. Resonances are reported in δ units downfield from the 0.03% tetramethylsilane (TMS) internal reference at 0.0 ppm.

Gas chromatography was carried out on a Hewlett Packard 5880A series equipped with an FID detector and a fused silica 0.31 mm x 50 m capillary column packed with a 0.17 mm film of SE-54 (methylphenylsilicone). Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, Georgia, or by University of Florida Spectroscopy Services. Mass spectral data were recorded on a Finnigan MAT 95Q or Finnigan MAT GCQ Gas Chromatograph/Mass Spectrometer under CI or EI conditions.

Thermogravimetric Analysis (TGA) data were recorded on either a Perkin Elmer Thermal Analysis Series 7 System interfaced to a TGA7 Thermogravimetric Analyzer, or on a DuPont 2000 Thermal Analysis System interfaced to a HIRES TGA 2950 Thermogravimetric Analyzer. All TGA samples were performed under air and nitrogen with a flow rate of 40 mL/min and program heating from 25-1000 °C at 10 °C/min.

Gel Permeation Chromatography (GPC) data were recorded using a Waters Associates Liquid Chromatograph U6K system, equipped with a tandem ABI Spectroflow 757 UV absorbance detector and a Perkin-Elmer LC-25 RI detector. All

molecular weights are relative to polybutadiene or polystyrene standards. Polymer samples were prepared in $CHCl_3$ (1% w/w), passed through a 50 μm filter, and injected (20 μL) successively through 5 x 10^3 Å and 5 x 10^4 Å Phenogel columns (crosslinked polystyrene gel) at a flow rate of 1 mL/min. Retention times were calibrated against polystyrene standards (Scientific Polymer Products, Inc.) or polybutadiene standards (Polysciences, Inc.). The molecular weights of the polystyrene and polybutadiene standards used were the following: PS(M_p) = 1900, 7700, 12000, 30000, 48900, 59000, 79000, 139400, 650000; PB(M_w) = 439, 982, 2760, 24000, 110000. All polydispersities (M_w/M_n) of the polymer standards used were less than 1.07.

Materials and Techniques

A mixture of tungsten hexachloride (WCl_6, Aldrich, 99.9+%) and diethylaluminum chloride (Et_2AlCl, Aldrich, 1.8 M in toluene) (1) was used as a classical metathesis catalyst system. The preformed metathesis alkylidenes employed in this research were previously developed in the laboratories of Schrock and Grubbs. The molybdenum version of Schrock's alkylidene, Mo(CHR')(NAr)$(OR)_2$ (2) where Ar = 2,6-(i-Pr)$_2$-C_6H_3, R' = $C(CH_3)_2Ph$, and R = $CCH_3(CF_3)_2$, was synthesized according to published literature methods.[47,85-89] Grubbs' ruthenium catalysts, $RuCl_2$(=CHR)$(PR_3)_2$, where R = cyclohexyl (3) or phenyl (4), were generously provided by Mark Watson, Shane Wolfe, Dr. John David Anderson, and Lauri Jenkins via the literature procedure[90] and through communications with the Grubbs group at the California Institute of Technology, Pasadena, CA. All catalyst systems employed in this study are shown in Figure 2.1.

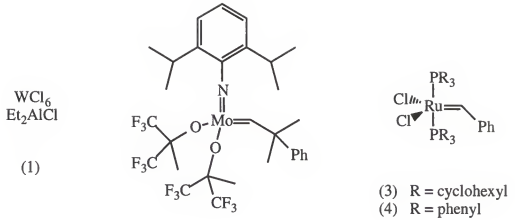


Figure 2.1. Classical catalyst 1, Schrock's molybdenum alkylidene 2, and Grubbs' ruthenium alkylidenes 3 and 4.

All monomer and catalyst manipulations were conducted either in an argon glove box or under standard Schlenk conditions. Toluene used in polymerizations was freshly distilled from NaK and stored under argon in a round bottom flask equipped with a high vacuum Teflon™ valve. Metathesis polymerizations were conducted in Teflon™ capped vials containing a magnetic stir bar in an argon dry box. All monomers (0.1 - 2.0 g) were added to the vials in the dry box where the appropriate catalyst (2 - 20 mg) was introduced. Exact monomer to catalyst ratios are discussed below. Polymerizations initiated by the classical catalyst system were quenched by exposure to air. Polymers formed from the Schrock alkylidene initiator were terminated by the addition of purified benzaldehyde.[91] Polymers were isolated by precipitation from toluene/methanol or chloroform/methanol prior to characterization.

8,9-Dihydrodicyclopentadiene (5) was purchased from Wiley Organics (99%) and used as received. 5,6-Dihydrodicyclopentadiene (6) was purchased from TCI (95+%) and was sublimed prior to use. Norbornene (Acros, 99%) was vacuum transferred to a Schlenk tube prior to use. 1,9-Decadiene (Aldrich, 98%) was dried over CaH_2, followed by vacuum transfer from a potassium mirror prior to use. All monomers were stored

under argon in high vacuum storage flasks equipped with Teflon™ valves or in Teflon™ capped vials in the dry box.

Dicyclopentadiene (9) was purchased from Aldrich (95% minimum, 90/10 *endo*/*exo*) and further purified as described in the literature[92] prior to use. Dicyclopentadiene was placed in a round bottom flask equipped with a magnetic stirring bar and a Teflon™ rotoflow valve. The flask was heated at 100 °C at 90-100 mm Hg for thirty minutes, or until the evolution of low boiling impurities was no longer detected. Activated molecular sieves were added after cooling under an argon purge, and the flask sealed. The dicyclopentadiene had solidified upon standing overnight, mp = 32 °C indicating that the compound was pure.[93] Spectral characteristics of the purified 9 agree with those published in the literature.[94]

Synthesis and Characterization

Olefin Reactivity Study

Synthesis of 5,6-dihydrodicyclopentadiene (6)

Standard literature procedures for diimide reductions were modified for this synthesis.[95-97] Dicyclopentadiene (5.0 mL, 37 mmol), triethylamine (10.3 mL, 74 mmol, Aldrich), *p*-toluenesulfonhydrazide (13.7 g, 74 mmol, Aldrich), and 50 mL toluene were place in a 3-necked round bottom flask equipped with a magnetic stirbar, reflux condenser, and argon inlet. The reaction mixture was heated at 100 °C for two hours with stirring while evolution of nitrogen was observed. Following this period, the mixture was heated at a gentle reflux for four hours, then cooled under argon. The organic layer was washed twice with water and twice with saturated potassium carbonate, then dried over anhydrous magnesium sulfate. Toluene was removed under vacuum, and

the reaction mixture was further purified by column chromatography, eluting with hexane. Product 6 was isolated as white crystals, mp 45-47 °C, in less than 5% yield. Literature mp 46-47 °C.

^{1}H NMR: δ 5.58 (m, 2H), 1-3 (m, aliphatic protons, 12H).

Alternate synthesis of 5,6-dihydrodicyclopentadiene (6)

A 100 mL round bottom flask, equipped with a magnetic stirring bar and a vacuum/argon adapter, was flame dried and cooled under vacuum. The flask was flushed with argon, the charged with 10% palladium on carbon (30 mg) and methanol (50 mL). The argon atmosphere was replaced by hydrogen, and the pressure was allowed to stabilize. Dicyclopentadiene (5.0 mL,37 mmol) was added to the flask, stirring was initiated, and hydrogen uptake was observed. A total of 850 mL (37.9 mmol) of hydrogen was added. The reaction mixture was filtered through a glass frit to remove the charcoal, and the methanol was removed under vacuum. After recrystallization from cold methanol, product 6 was isolated as white crystals, mp 45-47 °C, in 70% yield. Analysis by GC showed purity of >99%.

^{1}H NMR: δ 5.58 (m, 2H), 1-3 (m, aliphatic protons, 12H). GC/MS: m/z = 134.040.

Synthesis of poly(8,9-dihydrodicyclopentadiene) (7) with classical catalyst 1

8,9-Dihydrodicyclopentadiene (5) (0.2 g, 1.5 mmol) was placed in a clean vial equipped with a magnetic stirring bar. Toluene (4 mL) and WCl_6 (10 mg) were added. After stirring was initiated, Et_2AlCl (0.1 mL, 1.8 M in toluene) was added, and polymerization was complete, as indicated by complete solidification of the mixture, in

under 25 seconds. Polymer 7 was dissolved in toluene and precipitated from cold methanol.

^{1}H NMR: δ 5.4 (d), 2.8 (m), 2.5 (m), 1.6 (broad s), 1.2 (m).

Synthesis of poly(8,9-dihydrodicyclopentadiene) (7) with molybdenum catalyst 2

8,9-Dihydrodicyclopentadiene (5) (0.2 g, 1.5 mmol) was placed in a clean vial equipped with a magnetic stirring bar. Dry toluene (4 mL) was added and stirring was initiated. Molybdenum catalyst 2 (10 mg) was added, and polymerization immediately ensued, as indicated by the increased viscosity of the solution. Polymer 7 was dissolved in fresh toluene and precipitated from cold methanol.

^{1}H NMR: δ 5.4 (d), 2.8 (m), 2.5 (m), 1.6 (broad s), 1.2 (m).

Synthesis of poly(5,6-dihydrodicyclopentadiene) (8) with classical catalyst 1

Freshly sublimed 6 (0.1 g, 0.75 mmol) was placed in a Schlenk tube equipped with a magnetic stirring bar. Dry toluene (2 mL) and WCl_6 (10 mg) were added and stirring was initiated. Diethylaluminum chloride (0.1 mL, 1.8 M in toluene) was added to the Schlenk tube, and the reaction was allowed to stir for two days. The polymerization was quenched by exposing the mixture to air and filtering through a bed of alumina to remove catalyst. Toluene was removed under vacuum, and the polymer 8 was precipitated from cold methanol.

^{1}H NMR: all aliphatic peaks: δ 3.1 (m), 2.9 (m), 2.5 (m), 2.3 (d), 2.1 (d), 1.9 (m), 1.6 (m), 1.4 (m). GPC results (versus polybutadiene standards): M_n=3000 g/mol, M_w=3700 g/mol, M_w/M_n=1.23.

Attempted synthesis of poly(5,6-dihydrodicyclopentadiene) (8) with molybdenum catalyst 2

In an argon dry box, freshly sublimed 6 (0.1 g, 0.75 mmol) was placed in a clean vial equipped with a magnetic stirring bar, and dry toluene (2 mL) was added to dissolve monomer. Molybdenum catalyst 2 (10 mg) was added, and the reaction was allowed to stir for two days. The vial was removed from the dry box and the reaction was quenched by exposing to air and filtering the reaction mixture through a bed of alumina. Solvent was reduced by vacuum, and the reaction mixture was poured into cold methanol, where no precipitate was observed. Solvent was removed and only starting material was observed by GC and ^{1}H NMR.

Attempted bulk synthesis of poly(5,6-dihydrodicyclopentadiene) (8) with molybdenum catalyst 2

In a dry box, freshly sublimed 6 (0.1 g, 0.75 mmol) was placed in a clean vial equipped with a magnetic stirring bar, and a minimum amount of dry toluene was added to give a homogeneous reaction medium. Molybdenum catalyst 2 (10 mg) was added, and the mixture was allowed to stir for two days. The vial was removed from the dry box and the reaction was quenched by exposing to air and filtering the reaction mixture through a bed of alumina. The reaction mixture was poured into cold methanol, where no precipitate was observed. Solvent was removed and only starting material was observed by GC and ^{1}H NMR.

Attempted synthesis of poly(5,6-dihydrodicyclopentadiene) (8) with molybdenum catalyst 2 at low temperature

In an argon dry box, monomer 6 (1 g) was placed in a Schlenk tube with a magnetic stir bar and 0.5 mL dry toluene. Catalyst 2 (10 mg) was added and the tube was removed from the dry box and cooled to -40 °C under an argon purge. The mixture was stirred for 1 hour, then 0.5 mL benzaldehyde was added to endcap any polymer which may have formed, and quench the catalyst. The mixture was stirred at -40 °C for 30 minutes, then the tube was warmed to room temperature. The mixture was poured into cold methanol to precipitate any polymer which may have formed. No precipitate was observed, so solvent was evaporated. The resultant residue was analyzed by ^{1}H NMR, and only unreacted starting material was observed.

Attempted synthesis of poly(5,6-dihydrodicyclopentadiene) (8) with molybdenum catalyst 2 at elevated temperature

Monomer 6 (1 g) was placed in a clean Kontes flask equipped with a magnetic stirring bar in the drybox. A few drops of dry toluene were added to dissolve the monomer. Molybdenum catalyst 2 was added, and the flask was sealed. After removing from the drybox, the flask was heated at 100 °C while the solution was stirred. After two hours, the toluene was evaporated and the residue analyzed. ^{1}H NMR showed no sign of reaction between monomer and catalyst. Only starting material was observed.

Attempted NMR scale reaction of 5,6-dihydrodicyclopentadiene (6) with molybdenum catalyst 2

An approximately 5:1 molar ratio of 5,6-dihydrodicyclopentadiene (6) to molybdenum catalyst 2 was dissolved in 1 mL $CDCl_3$ and placed in a Teflon™ valve capped NMR tube. No change was observed in the alkylidene peak for catalyst 2, indicating that no metathesis exchange had occurred. The intensity of the alkylidene signal remained constant for more than two hours, demonstrating that catalyst decomposition did not occur.

Attempted synthesis of poly(5,6-dihydrodicyclopentadiene) (8) with ruthenium catalyst 3

5,6-Dihydrodicyclopentadiene (6) (0.5 g) was placed in a clean vial equipped with a magnetic stirring bar. A few drops of dry toluene were added to dissolve the monomer. Ruthenium catalyst 3 (10 mg) was added, and the solution was stirred for three hours. Toluene was evaporated, and the resultant residue was analyzed. ^1H NMR showed no evidence of reaction between the monomer and the catalyst. Only starting material was observed.

Attempted synthesis of poly(5,6-dihydrodicyclopentadiene) (8) with ruthenium catalyst 4

5,6-Dihydrodicyclopentadiene (6) (0.5 g) was placed in a clean vial equipped with a magnetic stirring bar. A few drops of dry toluene were added to dissolve the monomer and give a homogeneous reaction medium. Ruthenium catalyst 4 (10 mg) was added, and the solution was stirred for three hours. Toluene was evaporated, and the resultant residue was analyzed. ^1H NMR showed no evidence of reaction between the monomer and the catalyst. Only starting material was observed.

Attempted NMR scale reaction of 5,6-dihydrodicyclopentadiene (6) with ruthenium catalyst 3

An approximately 5:1 molar ratio of 5,6-dihydrodicyclopentadiene (6) to ruthenium catalyst 3 was dissolved in 1 mL $CDCl_3$ and placed in a Teflon™ valve capped NMR tube. No change was observed in the alkylidene peak for catalyst 3, indicating that no metathesis exchange had occurred. The intensity of the alkylidene signal remained constant for more than two hours, demonstrating that catalyst decomposition did not occur.

Attempted copolymerization of 5,6-dihydrodicyclopentadiene (6) and 1,9-decadiene

Monomer 6 (0.1 g, 0.74 mmol) and 1,9-decadiene (0.5 g, 3.6 mmol) were placed in a clean vial in an argon dry box with a magnetic stir bar. Stirring was initiated, and catalyst 2 was added. Immediate evolution of ethylene was observed. Stirring was continued for 30 minutes, after which time the waxy solid was removed from the dry box. The polymer was dissolved in methylene chloride and precipitated from cold methanol. The polymer was filtered and dried prior to analysis. ^{1}H and ^{13}C NMR were consistent with the formation of only polyoctenamer. There was no indication of incorporation of monomer 6 into the polymer.

Attempted copolymerization of 5,6-dihydrodicyclopentadiene (6) with norbornene

In an argon dry box, 5,6-dihydrodicyclopentadiene (6) (0.1 g, 0.74 mmol) and norbornene (0.5 g, 5.3 mmol) were dissolved in dry toluene (1 g). The solution was stirred and molybdenum catalyst 2 (5 mg) was added. The viscosity of the solution

visibly increased after the polymerization had started. The reaction was allowed to continue in the dry box overnight. Dry benzaldehyde (5 drops) was added to quench the catalyst. The solution color changed from gold to green within a few minutes. The polymer was precipitated from cold methanol and dried prior to characterization. Spectroscopic analysis by ^{1}H and ^{13}C NMR indicated that only polynorbornene was formed in the reaction.

Attempted copolymerization of 8,9-dihydrodicyclopentadiene (5) and 5,6-dihydrodicyclopentadiene (6)

In a vial in an argon dry box, 8,9-dihydrodicyclopentadiene (5) (0.5 mL, 3.7 mmol) and freshly sublimed 5,6-dihydrodicyclopentadiene (6) (.2 g, 1.5 mmol) were dissolved in 0.5 mL dry toluene. The solution was stirred, and catalyst 2 (5 mg) was added. The reaction was allowed to stir in the drybox overnight. After removing the vial from the dry box, the viscous solution was poured into cold methanol. The precipitated polymer was dried prior to characterization. ^{1}H NMR of the sample was consistent with that of homopolymer 7. There was no indication that monomer 6 had been incorporated into the polymer.

Thermal oligomerization of 5,6-dihydrodicyclopentadiene (6)

Freshly sublimed 6 (1.0 g, 7.5 mmol) was added to a Kontes flask equipped with a magnetic stirring bar. The flask was evacuated and purged with argon multiple times to ensure an inert atmosphere. Dry toluene (0.5 mL) was added via syringe to facilitate washing of any sublimed monomer back into the reaction mixture. The flask was sealed under argon and immersed in an oil bath at 160 °C for four hours. The reaction mixture was allowed to cool, and the liquid was placed on a watch glass to evaporate. The

residue was transferred to a Schlenk tube and evacuated for 4 hours to remove residual monomer, giving a final overall yield of less than 5%. The resulting residue 10 was analyzed by GC/MS and found to be mainly monomer with components with m/z = 268.080 and 402.120.

^{1}H NMR: δ 0.8 - 3.0 (aliphatic), 5.5 (olefinic), integration approximately 60:2 (aliphatic to olefinic).

Polymerization Crosslinking Studies

Bulk synthesis of polydicyclopentadiene with classical catalyst 1

In an argon drybox, tungsten hexachloride (10 mg, 0.03 mmol) was dissolved in a few drops of dry toluene in small beaker. Dicyclopentadiene (2 mL, 15 mmol) was added to the beaker, and stirring was initiated. After a few moments, diethylaluminum chloride (0.5 mL, 1.8 M in toluene) was added, and reaction ensued immediately. Vapors of monomer and solvent were observed condensing on the walls of the beaker. A dark black-brown polymer formed, which was insoluble in chloroform, toluene, *o*-xylene, and 1,2,4-trichlorobenzene, and could not be further characterized.

Bulk synthesis of polydicyclopentadiene with classical catalyst 1 in the presence of acetylacetone

In an argon drybox, tungsten hexachloride (10 mg, 0.03 mmol) was dissolved in a few drops of dry toluene in small beaker. Dicyclopentadiene (2 mL, 15 mmol) and acetylacetone (15 mg, 0.15 mmol) were added to the container, and stirring was initiated. Diethylaluminum chloride (0.5 mL, 1.8 M in toluene) was added, and after about 5

minutes, the formation of a gel was observed. Vapors of monomer and solvent were observed condensing on the walls of the beaker. A dark brown polymer formed, which was insoluble in chloroform, toluene, *o*-xylene, and 1,2,4-trichlorobenzene, and could not be further characterized.

Bulk synthesis of polydicyclopentadiene with molybdenum catalyst 2

Purified dicyclopentadiene (2 mL, 15 mmol) was placed in a clean vial with a few drops of toluene. Catalyst 2 (10 mg, 0.013 mmol) was added and the vial was swirled to mix reactants. The solution appeared to form a gel after a few minutes. Solid polymer was observed after reacting overnight. Samples of 10 were placed in Soxhlet extractors and extracted with toluene and *o*-xylene for two days, where partial dissolving was observed. A sample was also placed in 1,2,4-trichlorobenzene at 200 °C for two days, after which the sample was mostly dissolved. The soluble fractions were subsequently poured into cold methanol, precipitating the linear polymer. Samples were dried under vacuum prior to analysis.

^{1}H NMR: δ 5.68 (broad s), 5.55 (broad s), 5.32 (broad m), 1-3.4 (broad aliphatic peaks). GPC data: toluene fraction: M_n = 50,000 g/mol, M_w = 116,000 g/mol, M_w/M_n = 2.3; *o*-xylene fraction: M_n = 22,500 g/mol, M_w = 95,000 g/mol, M_w/M_n = 4.2; 1,2,4-trichlorobenzene fraction: M_n = 52,000 g/mol, M_w = 125,000 g/mol, M_w/M_n = 2.4.

Solution polymerization of dicyclopentadiene with molybdenum catalyst 2

Purified dicyclopentadiene (1 g, 7.5 mmol) was placed in a clean vial equipped with a magnetic stirring bar, followed by the addition of 10 grams toluene. Stirring was initiated, and catalyst 2 (10 mg) was added. The viscosity of the solution appeared to increase after a few minutes. Polymerization was allowed to continue for 12 hours, after

which the solution was poured into cold methanol, and linear polymer 11 was isolated. Polymer 11 was completely soluble in common organic solvents.

^{1}H NMR: δ 5.68 (broad s), 5.55 (broad s), 5.32 (broad m), 1-3.4 (broad aliphatic peaks). GPC data (in chloroform): M_n = 52,000 g/mol; M_w = 116,000 g/mol; M_w/M_n = 2.23. TGA: T_{10} = 448 °C.

Solution polymerization of dicyclopentadiene with molybdenum catalyst 2 at reduced temperature

Purified dicyclopentadiene (1 g, 7.5 mmol) was placed in a clean Schlenk tube equipped with a magnetic stirring bar, followed by the addition of 2 grams toluene, yielding a solution concentration of 2.28 M. The solution was cooled to -78 °C under an argon purge, and stirring was initiated. Catalyst 2 (10 mg) was dissolved in a minimum amount of toluene and transferred to the flask via cannula. The reaction mixture was allowed to warm slowly to room temperature overnight. After precipitation from cold methanol, the resulting polymer 11 was readily soluble in common organic solvents. Polymer yield: 0.2 g (20%).

GPC data (in chloroform): M_n = 28,000 g/mol; M_w = 47,000 g/mol; M_w/M_n = 1.69. ^{1}H NMR analysis agrees with that given for solution polymerization.

Bulk synthesis of polydicyclopentadiene (12) with ruthenium catalyst 3

In an argon drybox, dicyclopentadiene (9) (1 mL, 7.5 mmol) was placed in a clean vial equipped with a magnetic stirring bar. A minimum amount of dry toluene was added to yield a homogeneous reaction mixture and stirring was initiated, then ruthenium catalyst 3 (10 mg) was added. The solution initially had a violet purple color, which faded to a brown-red after a few minutes. The solution eventually lost all red color and

turned to a cloudy gray. After about two hours of reaction time, the entire mass had formed a waxy, insoluble gel (12) that was unable to be further characterized.

Solution synthesis of polydicyclopentadiene (12) with ruthenium catalyst 3

Dicyclopentadiene (9) (1 mL, 7.5 mmol) was placed in a clean vial equipped with a magnetic stirring bar. Dry toluene (10 mL) was added and stirring was initiated, then ruthenium catalyst 3 (10 mg) was added. The solution initially had a violet purple color, which faded to a brown-red after a few minutes. The solution eventually lost all red color and turned to a cloudy gray. After about two hours of reaction time, the entire mass had formed a waxy, insoluble gel that was unable to be further characterized.

Synthesis of polydicyclopentadiene with ruthenium catalyst 3 in the presence of n-propyl acetate

The solution polymerization of dicyclopentadiene was carried out as described above using ruthenium catalyst 3. In this case, n-propyl acetate (5 mg, 0.05 mmol) was added as a Lewis base to circumvent any Lewis acid catalyzed processes, as based on a literature procedure.[98] The solution remained transparent for about 15 minutes, then became cloudy and eventually opaque. An insoluble polymer gel (12) was formed in the reaction. The presence of n-propyl acetate had no apparent effect on the polymerization. Polymer 12 was unable to be characterized.

Synthesis of polydicyclopentadiene with ruthenium catalyst 3 in the presence of *p*-methoxyphenol

The solution polymerization of dicyclopentadiene was carried out as described above using ruthenium catalyst 3. In this case, *p*-methoxyphenol (89 mg, 0.7 mmol) was added as an inhibitor to avoid any radical crosslinking processes, based on a literature procedure.[99] The solution remained transparent for about 15 minutes, then became cloudy and eventually opaque. An insoluble polymer gel (12) was formed in the reaction, and was unable to be further characterized. The presence of *p*-methoxyphenol had no apparent effect on the crosslinking reaction of polymer 12.

Solution synthesis of polydicyclopentadiene with ruthenium catalyst 4

Dicyclopentadiene (9) (1 mL, 7.5 mmol) was placed in a clean vial equipped with a magnetic stirring bar. Dry toluene (10 mL) was added, stirring was initiated, and ruthenium catalyst 4 (10 mg) was added. The solution initially had a violet purple color, which faded to a brown-red after a few minutes. The solution eventually lost all red color and turned to a cloudy gray. After about two hours of reaction time, the entire mass had formed a waxy, insoluble gel (13) that was unable to be further characterized.

Attempted crosslinking of linear 11 by gradual concentration

Polymer 11 was generated under solution polymerization conditions in a Schlenk tube as described above. After one hour of reaction time, conditions were kept inert, and the solvent was slowly removed under vacuum until solid polymer 11 was obtained. Toluene (ca. 5 mL) was added to the tube, and the polymer completely dissolved within

five minutes, indicating that no crosslinking had occurred. The toluene solution was poured into cold methanol, and polymer 11 precipitated.

Thermal crosslinking of linear polymer 11

Polymer 11 was generated under solution polymerization conditions in a Schlenk tube as described above. After reacting for one hour under argon, solvent was slowly stripped away under vacuum to reduce the volume by approximately two-thirds. The tube was purged with argon and placed in an oil bath at 180 °C. Immediate gelation of the solution was observed. After five minutes of heating, the tube was removed and cooled to room temperature. The polymer gel that was formed could not be dissolved in toluene at room temperature, or in 1,2,4-trichlorobenzene at elevated temperature (ca. 150 °C).

Synthesis of polydicyclopentadiene (11) endcapped with benzaldehyde

Solution polymerization of dicyclopentadiene (9) was carried out as described previously, with varying monomer/catalyst ratio in order to control chain length. After two hours of reaction time, dry benzaldehyde (15 mmol) was added to quench the catalyst. The solution color was observed to change from deep gold to dark green. Polymer 11 was precipitated from cold methanol and dried prior to further analysis or reaction.

Delayed crosslinking of polydicyclopentadiene (11) with classical catalyst 1

A sample of precipitated polymer 11 generated from initiation with catalyst 2 was dissolved in dry toluene in an argon blanketed vial. WCl_6 (30 mg) was added, followed

by addition of Et_2AlCl (0.1 mL, 1.8 M in toluene). After stirring for eight hours, the solids were filtered from solution and heated in 1,2,4-trichlorobenzene at 140°C. After four hours, the product remained insoluble, indicating that crosslinking had occurred. Insoluble polymer 14 could not be further characterized.

Attempted delayed crosslinking of polydicyclopentadiene (11) with molybdenum catalyst 2

A sample of precipitated polymer 11 generated from initiation with catalyst 2 was dissolved in various amounts of dry toluene in an argon drybox. A new portion of molybdenum alkylidene 2 was added, and the reactions were stirred overnight. After this time, the polymer remained completely soluble, indicating that crosslinking had not occurred.

Synthesis of bicyclo[3.3.0]octa-2,6-dione (15)

Bicyclo[3.3.0]octa-2,6-dione (15) was synthesized following the literature procedure.[100] A 1 L three-necked, round-bottomed flask was equipped with a thermometer, magnetic stirring bar, addition funnel, and condenser. Sodium hydroxide (11.73 g) and methanol (250 mL) were added to the flask and stirred. Once dissolution was complete, the flask was cooled and dimethyl 1,3-acetonedicarboxylate (50 g, 0.287 mol) was added dropwise with stirring, forming a pale yellow solution with white salts. The resulting slurry was heated to reflux, dissolving the salts, then aqueous 40% glyoxal (23.5 mL) was added with stirring at a rate to keep the temperature at 65 °C. The solution became deep orange and copious amounts of white salts formed. The salts were filtered and washed with methanol, then dried prior to further reaction. The yield of light yellow salt was 50.66 g.

The dried salts were placed in a 3 L Erlenmeyer flask with chloroform (450 mL) and water (350 mL), and stirred rapidly while two equivalents of chilled 1 M HCl (425 mL) were slowly added. The layers were separated and the aqueous layer was extracted three times with chloroform. The combined organic layers were combined and washed once with saturated NaCl, dried over anhydrous magnesium sulfate, and evaporated, yielding 32.67 g of the tetraester (61% overall).

A 1 L three-necked flask equipped with a magnetic stirring bar and a reflux condenser with a bubbler outlet was charged with the tetraester (32.67 g), 1 M HCl (150 mL), and glacial acetic acid (16.5 mL). The mixture was stirred rapidly and heated at reflux for about 2.5 hours, until evolution of carbon dioxide gad subsided. The solution was cooled in an ice bath and extracted with five portions of chloroform. The organic layers were combined, washed with saturated NaCl, dried over anhydrous magnesium sulfate, and evaporated. The crude white to light yellow diketone 15 was isolated in 52% overall yield, and recrystallized from ethanol (mp = 84-85 °C). Literature mp = 84-86 °C.

^{1}H NMR: δ 2.14 (d of d, 4H), 2.57 (d of d, 4H), 3.2 (m, 2H). Spectral characteristics agree with those published in the literature.[100]

Synthesis of bicyclo[3.3.0]octa-2,6-diol (16)

A 250 mL Erlenmeyer flask equipped with a magnetic stirring bar was charged with compound 15 (0.5 g, 3.8 mmol) and ethanol (5 mL). The mixture was stirred to dissolve the diketone, then cooled in an ice bath until small crystals were formed. At that time, a large excess of sodium borohydride (0.2 g, 5.3 mmol) was added with stirring. After fifteen minutes, water (10 mL) was added to stop the reaction. The mixture was acidified with 1 M HCl, and washed with five 20 mL portions ethyl acetate. The combined organic layers were dried and evaporated, yielding 0.324 g (64%) of crude product. The oil was used without further purification.

^{1}H NMR: δ 1.7 (m, 4H), 2.1 (m, 4H), 2.55 (m, 2H), 4.25 (m, 2H). Spectral charateristics agree with those publised in the literature for this compound.[101]

Synthesis of bicyclo[3.3.0]octa-2,6-diene (17)

The synthesis of compound 17 is based on published literature procedures.[101] A 250 mL three-necked round-bottomed flask was equipped with magnetic stirring bar, condenser, addition funnel, and vacuum/argon inlet. The apparatus was flame dried under vacuum and purged with argon prior to the addition of NaH_2 (0.48 g, 15 mmol) and dry ether (75 mL). The mixture was stirred while a solution of compound 16 (1.025 g, 7.2 mmol) in ether (10 mL) was added dropwise. The mixture was heated at reflux for three hours, after which time, CS_2 (1.52 g, 20 mmol) was added dropwise. After another three hours of reflux, CH_3I (2.84 g, 20 mmol) was added dropwise. Following the final three hours of reflux, the mixture was cooled to room temperature, transferred to a large Erlenmeyer flask, and quenched by the addition of water with stirring. The organic layer was separated and washed twice with water, once with saturated NaCl, and dried over $MgSO_4$ prior to evaporation. The crude viscous dark yellow oil was used without further purification.

The crude xanthate product was placed in a 50 mL round-bottomed flask attached to a dry ice coldfinger/vacuum transfer apparatus which had been purged with argon. The reaction mixture was heated in an oil bath to 180-190 °C. Upon reaching 180 °C, a gas was evolved, and a pale yellow liquid was obtained in the collection flask. The bicyclic diene 17 was formed, as indicated by GC/MS, in very low yield. GC/MS: m/z = 106 (calc. C_8H_{10} = 106). Spectral characteristics for this compound are described in greater detail in the literature.[101]

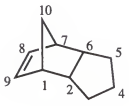
CHAPTER 3

OLEFIN REACTIVITY MODEL STUDY

The polymerization of dicyclopentadiene, as described in Chapter 1, has long been assumed to occur in two stages, where the initial formation of a linear polymer precedes a secondary metathesis reaction that leads to a crosslinked, insoluble material. Due to the inherent difficulties associated with analysis and characterization of crosslinked polymers, it is nearly impossible to understand the mechanisms which have actually operated to form this polymer. Although a mechanism of purely metathesis is assumed, some doubt remains due to the presence of ill-defined Lewis acid cocatalysts traditionally found in industrial polymerization systems. There is little question that metathesis polymerization occurs when highly strained monomers are exposed to these catalyst systems. However, Lewis acidic catalyst systems have been known to initiate cationic and addition processes, especially in the case of less strained rings.[73] It is for this reason that a model study which isolates the reactive olefins present in dicyclopentadiene was undertaken.

Dicyclopentadiene can be classified as a monomer possessing two sites of functionality, each one capable of reacting during polymerization leading to a crosslinked network polymer. With this in mind, two monofunctional compounds were chosen for a model study of olefin metathesis activity, as shown in Figure 3-1. The first compound, 8,9-dihydrodicyclopentadiene (5) (tricyclo[5.2.1.$0^{2,6}$]dec-8-ene), contains a norbornene type unsaturation, while an analogous compound, 5,6-dihydrodicyclopentadiene (6) (tricyclo[5.2.1.$0^{2,6}$]dec-3-ene), possesses a pendant cyclopentene. By choosing monomers with only one site of functionality, it is possible to generate linear polymers

which can be analyzed to determine the mechanism responsible for the polymerization, thus obviating the crosslinking problem. The reactivity of 8,9-dihydrodicyclopentadiene (5) towards ring-opening metathesis polymerization (ROMP) is expected to be much greater than that of 5,6-dihydrodicyclopentadiene (6) due to the larger amount of ring strain present in the bicyclic norbornene ring, as compared to the pendant cyclopentene.



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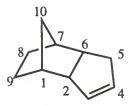


6

Figure 3-1. 8,9-Dihydrodicyclopentadiene (5) and 5,6-dihydrodicyclopentadiene (6) used in model study of olefin reactivity.

As discussed in Chapter 1, ring-opening metathesis polymerization is an equilibrium process, described by equation 3-1, where M denotes monomer and M_n is growing polymer chain. The equilibrium constant for the reaction is given in equation 3-2, and is defined as the ratio of polymer to growing polymer chains and monomer. Since the amounts of polymer and growing chains are essentially equal, these terms cancel, leaving K_{eq} as inversely proportional to monomer concentration. This equilibrium is ultimately governed by the Gibbs free energy equation (3-3).

$$M_n + M \underset{}{\overset{K_{eq}}{\rightleftharpoons}} M_{n+1} \qquad (3\text{-}1)$$

$$K_{eq} = \frac{[M_{n+1}]}{[M_n][M]} = \frac{1}{[M]} \qquad (3\text{-}2)$$

$$\Delta G = - RT \ln K_{eq} = \Delta H - T \Delta S \qquad (3\text{-}3)$$

As with most polymerization processes, there is a loss of entropy as monomer units are joined to form polymer, and ΔS for the system is negative (unfavorable). In order for high polymer to be obtained, the release of ring strain during the polymerization must be great enough such that the enthalpy term (ΔH) is exothermic, driving the reaction. If the magnitude of the enthalpy term is not great enough to offset the unfavorable effects of entropy loss, the equilibrium for the reaction will lie towards the reactants. Therefore, monomers which possess greater ring strain (larger, negative ΔH) are more likely to undergo ring-opening polymerization.

Comparing the model compounds 5 and 6 with similar structures of known ring strains, it can be seen that 8,9-dihydrodicyclopentadiene (5) should be much more likely to polymerize by ring-opening metathesis than 5,6-dihydrodicyclopentadiene (6). The reactive portion of monomer 5 is identical to that of norbornene, which has a ring strain of 27.2 kcal/mol.[102] On the other hand, the reactive part of monomer 6 is similar to cyclopentene, which shows a ring strain of 6.9 kcal/mol.[102] Monomer 6 can be assumed to be even more stable than cyclopentene since substitution in the ring reduces ring strain.[4]

A classical catalyst consisting of WCl_6/Et_2AlCl (1) was chosen to polymerize both model compounds in order to mimic the commonly used industrial polymerization systems for dicyclopentadiene, as illustrated in Figure 3-2. This catalyst system is representative of standard mixtures that lead to highly crosslinked polymers, which are discussed in greater detail in Chapter 1. When a catalyst system that contains a Lewis acid cocatalyst is used, there must be some concern that alternative reactions, other than olefin metathesis may occur, as these catalysts are not well-defined.[13] For this reason, both model monomers were also studied with Schrock's molybdenum alkylidene (2), which is known to only initiate metathesis reactions, without competing side reactions

that are commonly found in classical catalyst systems.[48] Grubbs' ruthenium alkylidenes (3 and 4) were also employed as preformed alkylidene catalysts for these model studies.

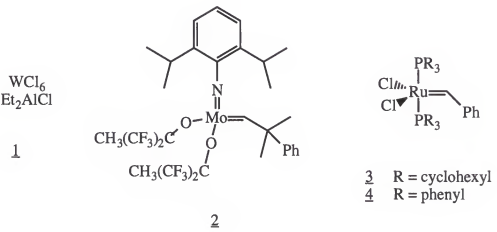


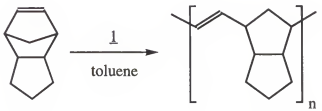
Figure 3-2. Classical catalyst system (1), Schrock's molybdenum alkylidene (2), and Grubbs' ruthenium alkylidenes (3 and 4) used for polymerization studies.

Polymerization of 8,9-Dihydrodicyclopentadiene

The model compound, 8,9-dihydrodicyclopentadiene (5), possesses a norbornene-type reactive moiety (see Figure 3-1), and therefore should behave in a similar manner to norbornene and form a metathesis ring-opened polymer. This general class of bicyclic monomers has been extensively studied,[4] and has been shown to be quite reactive towards ring-opening metathesis polymerization. It is postulated that the enthalpic release of ring strain energy in this system should be sufficient to allow exclusively ring-opening polymerization.

Classical Catalysis

Polymerization studies with 8,9-dihydrodicyclopentadiene (5) were conducted in the presence of classical catalyst system 1 to duplicate commonly used industrial catalyst systems. Compound 5 was dissolved in a minimum volume of toluene (enough to allow complete dissolution) followed by the addition of WCl_6. Once a homogeneous solution was obtained, the alkyl aluminum cocatalyst was added to generate the active catalyst *in situ* (Figure 3-3). Polymerization was rapid and exothermic, with the reaction going to completion, as indicated by the formation of solid product, in less than 30 seconds. The resultant poly(8,9-dihydrodicyclopentadiene) (7) was dissolved in toluene and precipitated from cold methanol prior to characterization. Polymer 7 remained completely soluble in common organic solvents such as toluene and chloroform.



5 7

Figure 3-3. Polymerization of 8,9-dihydrodicyclopentadiene (5) with classical catalyst system 1.

Poly(8,9-dihydrodicyclopentadiene) (7) was characterized by ^1H NMR to determine the primary structure of the polymer, thereby helping to understand the mode of polymerization (Figure 3-4). The presence of olefinic signals located at δ 5.4 indicated that ring-opening metathesis was an operative mechanism during the formation of polymer 7. These results were as expected and help to support the assumption that

ROMP of the strained bicyclic ring is the initial step that occurs during the polymerization of dicyclopentadiene.

If polymer 7 were formed exclusively by a ring-opening metathesis mechanism, integration of olefinic to aliphatic proton signals should yield a ratio of 2:12. The NMR analysis shown in Figure 3-4 revealed that the olefinic to aliphatic integrations were surprisingly in the ratio of approximately 2:23. This indicated that another mechanism was operating simultaneously with ring-opening metathesis, resulting in the disappearance of olefins during the polymerization. Formation of this second type of repeat unit is likely due to the presence of a Lewis acid cocatalyst in the system. Catalyst systems which employ Lewis acid cocatalysts have been previously shown to initiate cationic processes.[13]

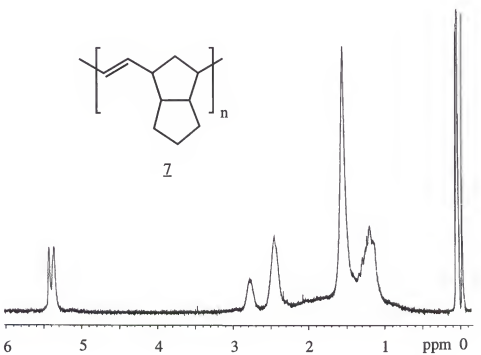
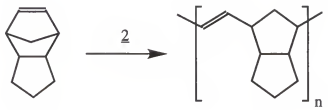


Figure 3-4. ^{1}H NMR of poly(8,9-dihydrodicyclopentadiene) (7) synthesized using classical catalyst 1.

If the integrations of the spectrum given in Figure 3-4 are taken to be representative of the structure of the polymer, it can be assumed that nearly half of the repeat units present in this system were formed via an olefin addition process. Although olefin addition has been observed before with WCl_6/Et_2AlCl and dicyclopentadiene,[73] the extent of vinyl chemistry was not as significant as what has been observed here for 8,9-dihydrodicyclopentadiene.

Well-Defined Catalysis

Due to the well-defined nature of the Schrock molybdenum alkylidene 2, it is reasonable to assume that an exclusive ring-opening metathesis mechanism would be expected for the formation of linear poly(8,9-dihydrodicyclopentadiene) (7) from monomer 5. This is indeed what has been observed. When 8,9-dihydrodicyclopentadiene was dissolved in a minimum amount of toluene and exposed to molybdenum catalyst 2, as described in Figure 3-5, linear polymer 7 formed immediately. The ^1H NMR spectrum shown in Figure 3-6 confirms that the polymers generated from both catalyst systems 1 and 2 are structurally similar, although the polymer produced from catalyst 2 is much "cleaner." An analysis of the integrations of the olefinic to aliphatic regions indicates a ratio of 2:12, exactly as expected for pure metathesis.



5 7

Figure 3-5. Polymerization of monomer 5 with molybdenum catalyst 2.

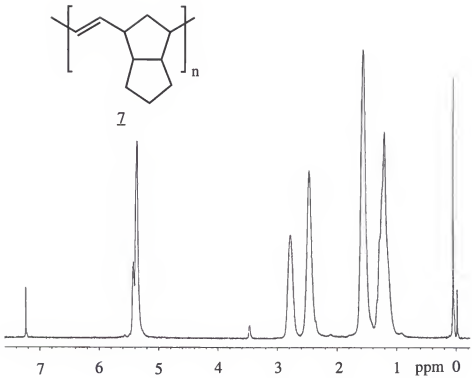


Figure 3-6. ^{1}H NMR spectrum of poly(8,9-dihydrodicyclopentadiene) (7) generated with molybdenum alkylidene 2.

The results described here for the polymerization of 8,9-dihydrodicyclopentadiene (5) with the well-defined molybdenum alkylidene 2 serve to illustrate the cleanliness of this system as compared to the classical system. There are no apparent side reactions observed for the molybdenum catalyst. This statement is not applicable to the classical system, where even a highly strained monomer which would normally be favored to undergo ring-opening metathesis polymerization reacted in another manner due to the presence of Lewis acidic components in the reaction mixture.

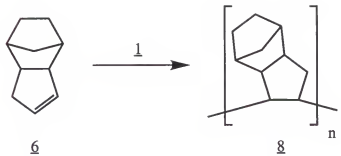
Polymerization of 5,6-Dihydrodicyclopentadiene

As mentioned earlier, it has long been assumed that the crosslinking reaction in the polymerization of dicyclopentadiene can be attributed to the metathesis of the pendant cyclopentenyl olefin. However, since the crosslinked polymer formed in this reaction cannot be fully characterized, it is only educated speculation which leads to this assumption. The results described in the previous section for monomer 5 have already suggested that olefin addition is a viable polymerization mechanism with the classical catalyst system. The purpose of the following experiments was to expose the cyclopentene moiety to both a classical catalyst system and a well-defined metathesis catalyst, in order to probe its reactivity.

Classical Catalysis

5,6-Dihydrodicyclopentadiene (6) was dissolved in a minimum amount of toluene and exposed to the classical catalyst system 1 for 24 hours to make a comparison with the industrial process used to generate polydicyclopentadiene, as described in Figure 3-7. This reaction afforded oligomers (8) with M_n = 3000 g/mol, and M_w/M_n = 1.23 as determined by GPC versus polybutadiene standards. This result was quite interesting, as it was contrary to the reports of Ofstead and Calderon, who stated that polymerization does not occur at all for this monomer with classical catalyst system 1.[65]

NMR analysis (Figure 3-8) of oligomer 8 unequivocally defined the nature of this polymerization system. Olefinic signals were no longer present in an appreciable extent in the ^1H NMR of oligomer 8, which ruled out ring-opening metathesis as a reaction pathway and indicated that oligomer 8 formed via an olefin addition reaction. This result was important, as it provided some insight into the potential mechanism of crosslinking



6 8

Figure 3-7. Polymerization of 5,6-dihydrodicyclopentadiene (6) with classical catalyst system 1.

which may occur during the polymerization of dicyclopentadiene with a conventional classical system. Even though a significant amount of residual monomer was present after reaction, oligomers of substantial length were formed, indicating that olefin addition was a viable polymerization pathway for this monomer. These findings differ from the generally accepted speculation that dicyclopentadiene crosslinking occurs exclusively through ROMP chemistry.

Lewis acid compounds, including metal halides, organometallic derivatives, and oxyhalides, are often used as initiators for cationic polymerization. The initiation usually proceeds faster if a proton source, such as an alcohol or water, is present in the system. Cationic polymerizations initiated by alkyl aluminum compounds are well known; in fact, $AlCl_3$ is the most widely used initiator for industrial cationic polymerizations.[52] The activity of aluminum compounds for cationic initiation generally corresponds to their order of Lewis acidity, with $AlCl_3 > AlRCl_2 > AlR_2Cl > AlR_3$.[103-105]

An interesting point to note is that if all traces of moisture and oxygen are excluded from the polymerization system, no product is formed with 5,6-dihydro-dicyclopentadiene (6) and the classical catalyst system 1 since the polymerization system is "too clean." When freshly sublimed commercial 5,6-dihydrodicyclopentadiene (6) was

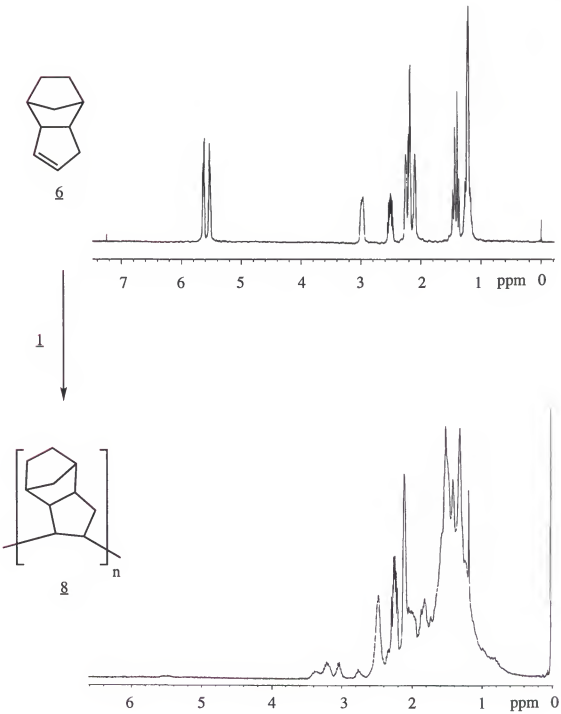


Figure 3-8. Oligomerization of 5,6-dihydrodicyclopentadiene (6) with classical catalyst 1.

exposed to WCl_6/Et_2AlCl in dry toluene, no reaction occurred. However, when 5,6-dihydrodicyclopentadiene (6) that was recrystallized from methanol is sublimed, then exposed to catalyst 1, oligomerization ensued. Evidently, a trace amount of methanol had survived the sublimation, allowing the reaction to proceed.

Another experiment, illustrated in Figure 3-9, was conducted to test this possibility. Two vials of pure 5,6-dihydrodicyclopentadiene (6) in dry toluene were made side by side. Pure, clean WCl_6/Et_2AlCl (1) was added to both vials, while 5 μL methanol was added to only one of the vials. After several hours of stirring, the mixtures were poured into cold methanol. Only the vial which had contained added methanol showed the formation of precipitate. These results help to explain why Ofstead and Calderon did not observe oligomer formation for 5,6-dihydrodicyclopentadiene. Their polymerization system must have been too clean for cationic initiation to proceed.

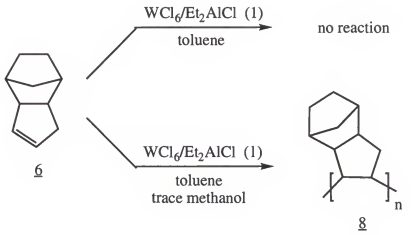


Figure 3-9. Comparison of the reaction of 5,6-dihydrodicyclopentadiene (6) with classical catalyst system 1 with and without trace methanol.

There is substantial precedence for this type of olefin addition chemistry, as the addition and cationic polymerizations of dicyclopentadiene and its derivatives have been extensively studied.[106-112] Exposing *endo*- and *exo*-dicyclopentadiene to a Pd(II)

catalyst has been shown to generate linear, non-crosslinked addition polymers with the unsaturation in the pendant ring remaining intact.[113] Linear oligomers of dicyclopentadiene have also been synthesized by Cesca and coworkers,[114] who studied the polymerization of dicyclopentadiene and its derivatives. Their results are consistent with the present discovery that oligomers are generated from 6 via an olefin addition process. The results discussed in the previous section for the polymerization of 8,9-dihydrodicyclopentadiene with classical catalyst system 1 also support these findings.

The generation of oligomers of 5,6-dihydrodicyclopentadiene via an olefin addition (likely cationic) process was a surprising and valuable result. As discussed in Chapter 1, disubstituted cyclopentenes, similar to the moiety present in monomer 6, have been shown not to undergo ring-opening metathesis polymerization at standard temperatures due to the lack of strain in the starting cycloolefin. It was therefore interesting to find another polymerization mechanism operating with this monomer. Consequently, exposing this monomer to a well-defined metathesis catalyst should provide additional information about the feasibility of ROMP for this system.

Well-Defined Catalysis

Based on the results generated from the oligomerization of 5,6-dihydro-dicyclopentadiene with the classical catalyst system 1, it was enticing to study the polymerization of 6 with a well-defined catalyst. The Schrock molybdenum alkylidene 2 has been shown to only initiate metathesis without generating by-products usually obtained with Lewis acid cocatalysts.[13] Since it has been previously reported that disubstituted cyclopentenes do not undergo ring-opening metathesis polymerization,[4] no metathesis would be expected to occur with this system.

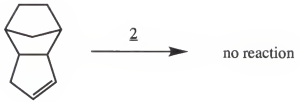
Substituents on a ring usually have an unfavorable effect on the ability of the monomer to polymerize by decreasing the ΔH value for the reaction. This is often a

result of changes in steric strain effect between the monomer and the polymer, where the linear, ring-opened polymer is thermodynamically less stable than the cyclic monomer. Combining equations 3-2 and 3-3, given earlier, yields the relationship described in equation 3-4, where T_c is ceiling temperature, $[M]_c$ is the equilibrium monomer concentration, and R is the ideal gas constant.

$$T_c = \frac{\Delta H}{\Delta S + R \ln [M]_c} \qquad (3\text{-}4)$$

The enthalpy change for the reaction (ΔH) and the ceiling temperature, T_c, are directly proportional. As a result, the unfavorable effect of ring substituents on ΔH of the reaction is translated to the ceiling temperature, lowering T_c relative to the unsubstituted monomer. The ceiling temperature of pure cyclopentene is estimated to be 97 °C.[115] Any substitution on the ring would cause this value to decrease dramatically. Therefore, disubstituted cyclopentenes are not able to be polymerized under standard metathesis conditions because these monomers are clearly above their ceiling temperatures for the concentrations examined.

The reactivity of 5,6-dihydrodicyclopentadiene (6) was examined with the well-defined metathesis alkylidene, 2. Monomer 6 was dissolved in a minimum amount of dry toluene to create a homogeneous reaction medium. Molybdenum catalyst 2 was added, and the mixture was stirred for two days at room temperature under argon to give ample time for reaction, as illustrated in Figure 3-10. After this time, the reaction mixture was poured into cold methanol to precipitate any polymer that may have formed. No precipitate was observed. The solvent was evaporated, leaving only the initial starting material. Repeated attempts to polymerize 6 using molybdenum catalyst 2 have resulted in the recovery of only unreacted starting material. Polymerization of 5,6-dihydro-dicyclopentadiene in the presence of 2 has also been attempted at -40 °C and 100 °C, but in each case, no polymer or metathesis product was formed.



6

Figure 3-10. Attempted polymerization of 5,6-dihydrodicyclopentadiene (6) with molybdenum catalyst 2.

When 5,6-dihydrodicyclopentadiene was exposed to catalyst 2 under NMR scale conditions, no change was observed in the alkylidene resonance, indicating that no exchange occurred between the catalyst and monomer. The intensity of the alkylidene signal remained unchanged for more than two hours, indicating that impurities did not poison the catalyst. These results indicate that monomer 6 is inert to metathesis polymerization with molybdenum alkylidene 2 under all conditions that were attempted.

In addition to examining the reactivity of this monomer with molybdenum alkylidene 2, 5,6-dihydrodicyclopentadiene (6) also was exposed to ruthenium catalysts 3 and 4 to determine the potential of these systems for ring-opening metathesis polymerization. With both of these catalysts, no reaction was observed, as described in Figure 3-11. Even under NMR scale conditions (high catalyst to monomer ratio), no exchange of monomer with alkylidene 3 was observed. These results help to support the argument that 5,6-dihydrodicyclopentadiene (6) is not polymerizable through metathesis ring-opening under standard metathesis reaction conditions.

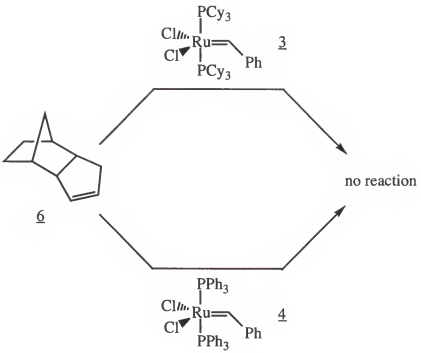


Figure 3-11. Attempted polymerization of 5,6-dihydrodicyclopentadiene (6) with ruthenium catalysts 3 and 4.

Copolymerization Attempts

Although there was little question while undertaking this model study that the pendant cyclopentene would not undergo metathesis polymerization with the well-defined molybdenum catalyst 2 or ruthenium catalysts 3 and 4, perhaps oligomers could be formed in the presence of an active alkylidene on a growing polymer chain. Therefore, if an active alkylidene could initiate polymerization of monomer 6, there should be some incorporation of 6 into the polymer. Several copolymerizations were attempted in order to test this possibility.

Monomer 6 was exposed to molybdenum catalyst 2 at room temperature in the presence of 1,9-decadiene, norbornene, and 8,9-dihydrodicyclopentadiene (5), as illustrated in Figure 3-12. In each of these cases, only homopolymer of the known

reactive monomers was obtained, with absolutely no indication by either ^{1}H or ^{13}C NMR that 6 had been incorporated into the polymer. This demonstrated that even in the presence of an actively metathesizing alkylidene, the olefin present in monomer 6 is not reactive to metathesis polymerization.

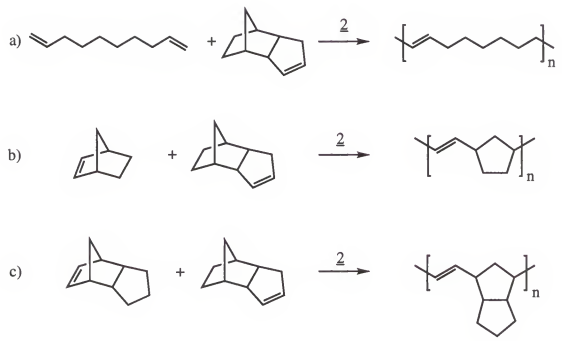


Figure 3-11. Attempted copolymerization of monomer 6 with various monomers. a) 1,9-decadiene, b) norbornene, and c) 8,9-dihydrodicyclopentadiene (5).

The results from these copolymerization studies are important because they lend support to the conclusion that disubstituted cyclopentenes, including 5,6-dihydrodicyclopentadiene (6), are inert to metathesis chemistry. The only successful polymerization chemistry that has been shown with compound 6 was the limited olefin addition as catalyzed with the classical Lewis acid cocatalyst system (1). No reaction was observed for 5,6-dihydrodicyclopentadiene (6) with either a well-defined metathesis initiator or an actively metathesizing polymer chain end.

Thermal Oligomerization of 5,6-Dihydrodicyclopentadiene

As discussed in Chapter 1, the crosslinking of dicyclopentadiene is often attributed to a secondary reaction in which the cyclopentene moiety of the monomer undergoes ring-opening metathesis to yield the final crosslinked polymer. However, the results described herein for the model studies with 5,6-dihydrodicyclopentadiene (6) indicated that this olefin was not reactive towards ring-opening metathesis, either under classical catalyst conditions, or with well-defined alkylidenes. Additionally, the results of Ofstead and Calderon with bicyclo[3.3.0]oct-2-ene indicated that this compound was also inert to metathesis.[65] Given that the repeat unit present in linear polydicyclopentadiene is identical in structure to bicyclo[3.3.0]oct-2-ene, as shown in Figure 3-13, it seems quite unlikely that crosslinking occurs through metathesis.

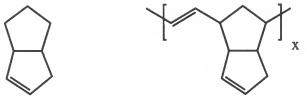


Figure 3-13. Similarities of bicyclo[3.3.0]oct-2-ene (left) to the repeat unit present in linear polydicyclopentadiene (right).

The amount of ring strain present in a cycloolefin, as discussed in Chapter 1, is often the determining factor of the reactivity of a given compound to ring-opening metathesis polymerization. ROMP reactions tend to be quite exothermic, especially for bicyclic monomers, with the release of ring strain causing a large increase in the temperature of the reaction mixture. These elevated temperatures could harbor additional competing side reactions which may lead to a crosslinked system. A control experiment

was conducted in which 5,6-dihydrodicyclopentadiene was heated in the absence of catalyst in order to demonstrate whether the crosslinking reaction of dicyclopentadiene could be thermally induced. After four hours of heating at 160 °C under argon, the flask was evacuated under normal Schlenk conditions to sublime away any unreacted 6 and the residue was characterized (Figure 3-14). GC/MS analysis of the reaction residue indicated that compounds with masses exactly two and three times that of monomer 6 were formed.

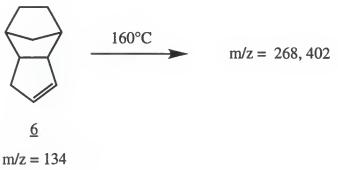


Figure 3-14. Thermal oligomerization of monomer 6 in the absence of catalyst.

^{1}H NMR analysis of the products, as given in Figure 3-15, showed a dramatic decrease in the olefinic region of the spectrum, where the integrations of the olefinic region compared to the aliphatic region were in the ratio of approximately 2:60, respectively. For this reason, it could be assumed that some process which consumed olefins was responsible for the formation of these dimers and trimers. Although only small molecules were made when compound 6 was heated, only a few crosslinks would be needed to yield an insoluble, gelatinous material during the polymerization of dicyclopentadiene. These results give evidence to support a thermally induced olefin addition reaction as the possible source for crosslinking in the polymerization of

dicyclopentadiene. Further, this thermal reaction may also be an operative crosslinking mechanism in conventional catalyst systems.

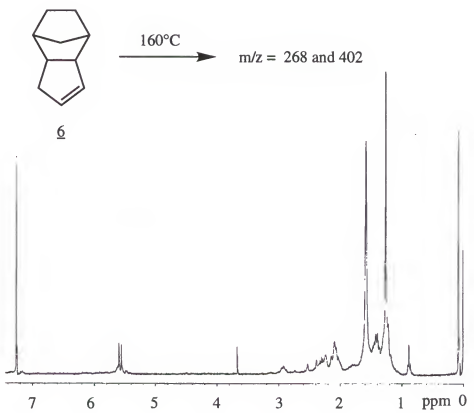


Figure 3-15. ^{1}H NMR of residue from thermally oligomerized 5,6-dihydro-dicyclopentadiene.

When considering a route for formation of dimers and trimers, one possibility is that during the period of heating monomer 6, an allylic hydrogen could have been abstracted from the cyclopentene moiety, generating an allylic radical. This radical could couple with the double bond of another molecule, forming the dimer with m/z = 268, and a structure similar to that depicted in Figure 3-16. This reaction could occur once again to yield the trimer with m/z = 402. This possible hydrogen atom abstraction would explain the formation of a product in which olefins were depleted.

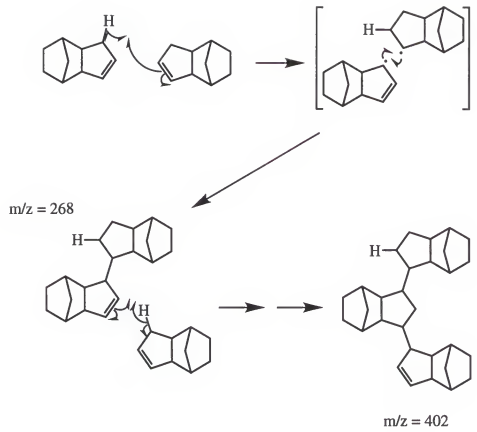


Figure 3-16. Proposed mechanism for formation of dimer (m/z = 268) and trimer (m/z = 402) generated from thermal reaction of 6 by allylic hydrogen atom abstraction.

An alternative mechanism which could lead to the formation of dimer and trimer of 5,6-dihydrodicyclopentadiene (6) is an intermolecular ene reaction, as illustrated in Figure 3-17. Although these reactions usually require higher temperatures, superheating during this model reaction, as well as localized heating during the polymerization of dicyclopentadiene, could have caused this reaction to occur. This pathway would also account for the depletion of olefins, as indicated by NMR analysis of the residue from heating monomer 6 (Figure 3-15).

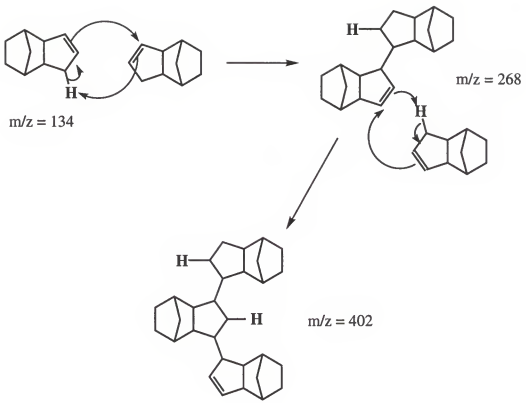


Figure 3-17. Proposed intermolecular ene reaction which may lead to the formation of 5,6-dihydrodicyclopentadiene dimer (m/z = 268) and trimer (m/z = 402).

Conclusions

The model studies with 8,9-dihydrodicyclopentadiene (5) and 5,6-dihydrodicyclopentadiene (6) have shown that these two compounds have quite different reactivities. Compound 5, with the norbornene-like double bond, undergoes facile metathesis to yield a ring-opened product instantly upon exposure to either the classical catalyst, WCl_6/Et_2AlCl (1), or the well-defined molybdenum catalyst, Mo(N-2,6-C_6H_3-*i*-Pr)(CHC$(CH_3)_2$Ph)(OC$CH_3(CF_3)_2)_2$ (2). Compound 6, with the fused cyclopentene moiety, appears to be nonreactive with the well-defined catalyst 2, as well as with the ruthenium catalysts Ru(CHPh)$Cl_2(PR_3)_2$, where R = cyclohexyl (3) or phenyl (4), yet

undergoes an olefin addition process when subjected to catalyst 1. These results were contrary to those previously published[65] which stated that 5,6-dihydrodicyclopentadiene did not polymerize, and are concrete evidence that olefin addition is a viable mechanism operating during the polymerization of dicyclopentadiene with classical Lewis acid cocatalyst systems. Additionally, dimers and trimers of 5,6-dihydrodicyclopentadiene have been formed from heating in the absence of any catalyst. With these results in hand, the next logical step would be to examine the polymerization of dicyclopentadiene with both the classical catalyst system and the preformed well-defined alkylidenes.

CHAPTER 4

CROSSLINKING STUDIES OF DICYCLOPENTADIENE

The polymerization of dicyclopentadiene has been known for more than 25 years, finding industrial utility for the manufacture of many types of impact resistant products. Polydicyclopentadiene that is generated from traditional classical catalyst systems is a tough, crosslinked material which is insoluble in organic solvents, making characterization difficult or nearly impossible. For this reason, many general assumptions have been made about the nature of the polymer that is formed during this reaction. There is no argument that the formation of the polydicyclopentadiene backbone occurs through the metathesis of the strained norbornene olefin; however, the method by which crosslinking occurs is still under debate.

Much of the information that is available for dicyclopentadiene polymerization is discussed in patent literature. These descriptions are typically of procedures, with little attention focused on mechanistic studies. Only a few researchers have attempted to determine the mode of crosslinking that occurs during the polymerization of dicyclopentadiene. Nearly thirty years ago, Dall'Asta and Montroni[73] studied the polymerization of dicyclopentadiene with classical catalysts by infrared spectroscopy and found various repeat units in the soluble fractions of their polymeric mixtures (see Figure 1-25 and Table 1-5 for details). Grubbs and coworkers[75,116] investigated the polymerization of dicyclopentadiene with tungsten and molybdenum based Schrock alkylidenes, and found that monomer concentration was critical for the formation of a crosslinked product. Although these studies helped to explain what could be happening

during the crosslinking reaction, conclusive information was limited due to the formation of insoluble networks which could not be characterized.

The model studies discussed in Chapter 3 of this dissertation serve to examine the individual reactivities of the olefins present in dicyclopentadiene toward ring-opening metathesis polymerization (ROMP), adding to the information previously known about this system. This chapter will focus on the polymerization of dicyclopentadiene with various catalyst systems, illustrated in Figure 4-1, in addition to a detailed account of several crosslinking studies that were conducted. By closely examining the conditions which do and do not lead to the formation of crosslinked polymers, better insight can be gained about the nature of these linkages.

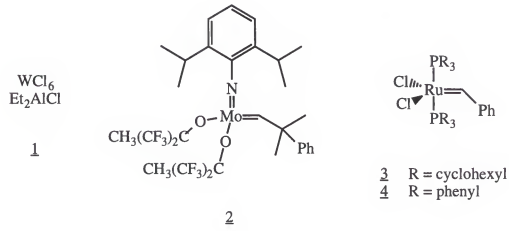


Figure 4-1. Classical catalyst system (1), Schrock's molybdenum alkylidene (2), and Grubbs' ruthenium alkylidenes (3 and 4) used for polymerization studies.

Polymerization of Dicyclopentadiene (9)

The results for the model study described in Chapter 3 with 8,9-dihydrodicyclopentadiene (5) and 5,6-dihydrodicyclopentadiene (6) begin a natural progression to the polymerization of dicyclopentadiene (9), as given in Figure 4-2. It is

reasonable to assume that the initial reaction that occurs during dicyclopentadiene polymerization is the linear ring-opening metathesis polymerization of the strained norbornene ring followed by another process which causes crosslinking. All attempts at the metathesis of model compound 6 with preformed molybdenum (2) and ruthenium (3 and 4) alkylidenes resulted in no reaction whatsoever. These results suggest that polymerization of dicyclopentadiene by these initiators should form linear, soluble polymer through the ring-opening metathesis polymerization of only the strained norbornene ring.

5

6

9

Figure 4-2. Structures for model compounds, 8,9-dihydrodicyclopentadiene (5) and 5,6-dihydrodicyclopentadiene (6), and dicyclopentadiene (9).

Classical catalyst systems are employed in most of the industrial polymerizations of dicyclopentadiene. The resulting polymers are typically crosslinked and insoluble in organic solvents,[117] which makes them impossible to characterize to determine the mechanisms by which they formed. It is proposed here that an alternative polymerization mechanism, olefin addition, is also occurring when classical catalysts are employed, and may be responsible for the formation of insoluble, crosslinked polymer.

Effects of Classical Catalysis

Initial investigations of the polymerization of dicyclopentadiene were conducted with the classical catalyst system of WCl_6/Et_2AlCl (1). This system was chosen because it is utilized industrially,[92] and is known to yield a highly crosslinked polymer. Polymerization of dicyclopentadiene with WCl_6/Et_2AlCl in a minimum amount of toluene (to simulate the industrial system) was quite rapid, generating a tough, insoluble sample in a matter of seconds, as illustrated in Figure 4-3. The amount of heat released during the reaction was quite large, with the condensation of solvent and monomer vapors evident on the walls of the reaction vessel.

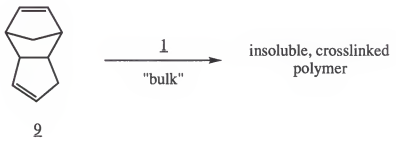


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Figure 4-3. Polymerization of dicyclopentadiene (9) with classical catalyst system 1.

A separate experiment was conducted where acetylacetone was added to slow the reaction. Usually, addition of either a Lewis basic component or a chelating agent moderates polymerization with classical catalysts by delaying the exotherm of the reaction. Acetylacetone chelates to the tungsten component, making the catalyst slightly less active. However, the addition of this moderator served only to slow the polymerization, while having little or no effect on the outcome of the reaction. The heat generated was just as intense, and the product was still dark and charred in appearance.

The polydicyclopentadiene generated in this reaction was completely insoluble in all solvents investigated, including refluxing chloroform, toluene, *o*-xylene, and 1,2,4-trichlorobenzene.

Preformed Alkylidenes

Following the investigations of the reactivity of dicyclopentadiene (9) with the classical catalyst system 1, the behavior of the monomer was studied with both Schrock's molybdenum alkylidene 2 and Grubbs' ruthenium alkylidenes 3 and 4. Preformed alkylidene catalysts by definition are more well-defined than classical catalyst systems, since the species responsible for metathesis is known. Additionally, a Lewis acid cocatalyst is not needed to render these initiators metathesis active. Considering that no reaction was observed for the pendant cyclopentene in the model compound, 5,6-dihydrodicyclopentadiene (6), it was expected that linear polymer could be formed with dicyclopentadiene.

Bulk polymerization with molybdenum alkylidene

The polymerization of dicyclopentadiene (9) was examined with the molybdenum alkylidene 2 as an essentially bulk system, where the monomer was dissolved in a minimum amount of toluene to simulate industrial polymerization conditions. When this sample of monomer 9 was exposed to molybdenum catalyst 2, as described in Figure 4-4, gelation of the sample was instantaneous. Based on the earlier results with 5,6-dihydrodicyclopentadiene (6), it should have been possible to generate linear polymer with the well-defined catalyst 2, since the pendant cyclopentene should not undergo metathesis. Given these results, the solubility of the polymer was examined to determine whether the gel was a consequence of crosslinking, or simply due to the speed of the

reaction, since high molecular weight, rigid polymer is generated during the initial stages of polymerization.

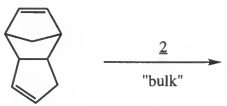

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Figure 4-4. Bulk polymerization of dicyclopentadiene (9) with molybdenum alkylidene 2.

Because of the high degree of polymerization and the rigidity of the insoluble polydicyclopentadiene (10) generated, it is possible that solubility may be limited, even though chemical crosslinks may not have been formed. Polymers which contain regular, rigid repeat units may often be solubilized by heating in an appropriate solvent. Toluene, *o*-xylene, and 1,2,4-trichlorobenzene were chosen as solvents because of the broad range of boiling points they offered (110 °C, 140 °C, and 214 °C respectively). A sample of 10 was placed in a Soxhlet extractor with refluxing toluene for two days, followed by extraction with *o*-xylene for two days. A second sample was heated in 1,2,4-trichlorobenzene for two days to see if any polymer would dissolve. GPC data based on polybutadiene standards was obtained from these soluble samples in order to determine their approximate molecular weights. The results are summarized in Table 4-1.

The polymer samples which resulted from bulk polymerization of dicyclopentadiene (9) with molybdenum catalyst 2 had only limited solubility in toluene, *o*-xylene, and 1,2,4-trichlorobenzene. This result indicated that some portion of the polydicyclopentadiene generated from molybdenum catalyst 2 was crosslinked. These

Table 4-1. Solubilities of bulk polymerization products 10 in various solvents.

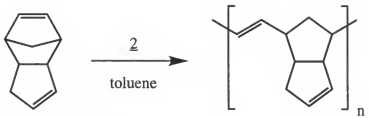
Solvent	Temperature	Sample Condition	Mn (GPC)†
toluene	110 °C	partially dissolved	50,000
o-xylene	140 °C	partially dissolved	22,500
1,2,4-trichlorobenzene	200 °C	mostly dissolved	52,000

†GPC results are for soluble portions only, given in g/mol.

findings raise questions about the mechanism which operated to form this polymer. Although metathesis of the pendant cyclopentene could be the mode by which the insoluble polymer is generated, this explanation is unlikely based on the results described in Chapter 3 for 5,6-dihydrodicyclopentadiene (6). Therefore, further investigations into the polymerization of dicyclopentadiene were necessary.

Concentration effects on solution polymerization with molybdenum alkylidene

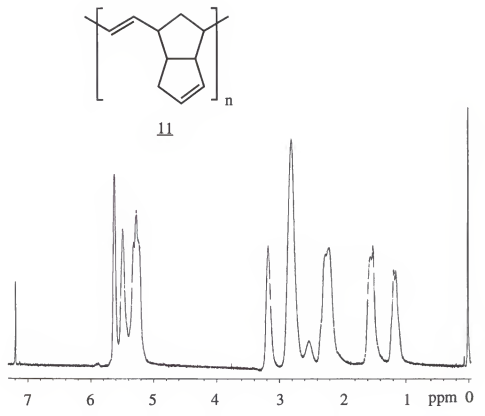
Dicyclopentadiene polymerization was studied in toluene solutions to make a comparison with the results generated from bulk polymerizations with the molybdenum alkylidene. Initial investigations of the polymerization of dicyclopentadiene in solution were conducted on 0.60 M samples (1 part monomer to 10 parts toluene) with molybdenum catalyst 2. After 24 hours of stirring under argon, the color of the solution remained deep golden yellow, and the polymer was completely soluble as expected. Polymer 11 (Figure 4-5) was precipitated from cold methanol and dried under vacuum prior to characterization by GPC and NMR. GPC analysis of polymer 11 (in chloroform versus polystyrene standards) shows an M_n = 52,000 g/mol and M_w/M_n = 2.2.



9 11

Figure 4-5. Solution polymerization of monomer 9 with molybdenum catalyst 2.

NMR analysis of polymer 11 confirmed that only the strained norbornene olefin undergoes metathesis during the polymerization, while the olefin in the pendant five-membered ring remains intact. Polymer 11 gives a ^{1}H NMR spectrum, shown in Figure 4-6, that is identical to that of linear polydicyclopentadiene generated using other catalyst systems. Various classical catalyst systems with weak Lewis acid cocatalysts were employed in these studies,[78,94] which are described in greater detail in the introduction of this dissertation. For those catalyst systems, as well as in this study with molybdenum catalyst 2, it is assumed that the absence of a strong Lewis acid cocatalyst removes the possibility for olefin destroying reactions, such as addition or cationic polymerization.



11

Figure 4-6. ^{1}H NMR of polymer 11 generated from solution polymerization of monomer 9 with molybdenum catalyst 2.

The result that high molecular weight, linear polydicyclopentadiene (11) can be obtained from molybdenum catalyst 2 is further supported by the fact that polymer 11 has been generated with a $M_n \approx$ 1,000,000 g/mol as determined by GPC, remaining completely soluble throughout the polymerization. This polymer was precipitated in cold methanol and was found to be readily soluble in chloroform and toluene, even after sitting for several days. These observations eliminated the possibility of crosslinking by metathesis through the less strained double bond.

After initial polymerizations of dicyclopentadiene were conducted with molybdenum catalyst 2 at a dilution of 1 part monomer to 10 parts toluene by weight, various concentrations were investigated to see if there might be a critical concentration above which the formation of insoluble polymer occurs. The results for these

experiments are summarized in Table 4-2. As the initial monomer concentration was increased, the formation of insoluble polymer was observed. It was an interesting result that soluble polymers could be generated at a dilution of 1:10 monomer to toluene, but when the concentration was increased to 1:9 monomer to toluene, an insoluble polymer was obtained. Like the bulk polymerization of dicyclopentadiene, polymers generated

Table 4-2. Concentration effects on polymer generated from dicyclopentadiene (9) on exposure to molybdenum catalyst 2.

Concentration (DCPD : toluene by weight)	Results
"bulk" (7.58 M)	low conversion, soluble polymer
1:1 (3.51 M)	insoluble gel
1:2 (2.28 M)	insoluble gel
1:9.5 (0.63 M)	insoluble gel
1:10 (0.60 M)	soluble polymer
1:>10 (<0.60 M)	soluble polymer

from solutions more concentrated than 0.60 M appeared to be crosslinked. These findings are inconsistent with the results of the model polymerization studies with 5,6-dihydrodicyclopentadiene (6), which indicated that metathesis crosslinking should not occur for dicyclopentadiene with Schrock's molybdenum alkylidene.

Fisher and Grubbs have conducted similar studies of the solution polymerization of dicyclopentadiene.[75] Their results show that high concentrations of dicyclopentadiene produce an insoluble material using Schrock's hexafluoro molybdenum catalyst (2). In keeping with the conventionally accepted theories, Fisher and Grubbs speculate that the formation of crosslinked polydicyclopentadiene is similar to the equilibrium ring-opening metathesis polymerization of cyclopentene. Perhaps when the concentration of the pendant cyclopentene units is high enough, ring-opening metathesis polymerization

would be possible. This reaction could be responsible for the formation of crosslinks in the final polydicyclopentadiene.

Although this assumption might make sense from an equilibrium concentration standpoint, inconsistencies are evident when the enthalpies of the reaction are considered. As discussed in Chapter 3, model polymerization studies with 5,6-dihydrodicyclopentadiene (6) have indicated that even at high monomer concentrations and low temperatures, no metathesis is observed for this compound with molybdenum alkylidene 2. Additionally, the reactivity of bicyclo[3.3.0]oct-2-ene (see Figure 3-13), a structure identical to the repeat unit found in linear polydicyclopentadiene, has been previously examined,[65] and this compound was also found to be inert to metathesis polymerization.

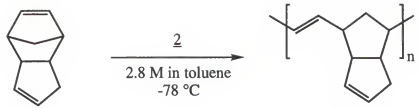
Effects of temperature on solution polymerization with molybdenum alkylidene

Another possible explanation for the formation of an insoluble polymer during the polymerization of dicyclopentadiene with Schrock's molybdenum alkylidene 2 could be attributed to the large amount of heat released during bulk polymerization. The ring-opening polymerization of the norbornene moiety is highly exothermic, as this unit possesses a ring strain of 27.2 kcal/mol.[102] When the polymerization of dicyclopentadiene is conducted in a less concentrated solutions, the solvent could potentially act as a heat sink, obviating the higher activation energy required for the olefin addition process. Therefore, crosslinking does not occur when polymerization is conducted in dilute solution.

As described in Chapter 3, dimers and trimers of the model compound, 5,6-dihydrodicyclopentadiene (6), can be generated through heating under inert conditions in the absence of any catalyst. A similar reaction might occur during the exotherm of the dicyclopentadiene polymerization when monomer concentration is high and heat is not

easily dissipated. If the release of heat from the ring-opening metathesis polymerization of the norbornene moiety is truly the cause of the crosslinking reaction, then prevention of the reaction exotherm should allow for the formation of linear, soluble polymer. This is evident in the solution polymerization studies presented above, where solvent can help to dissipate the heat released during the exotherm. Another way to prevent this exotherm would be to run the reaction at a low temperature. This would slow the polymerization dramatically and prevent the temperature of the reaction mixture from escalating.

The polymerization of dicyclopentadiene at low temperature was conducted in a 2.28 M toluene solution, a concentration which has been shown to yield an insoluble product at room temperature (see Table 4-2). By carrying out the polymerization at this concentration, it can be reasonably assumed that temperature would be the only variable to determine whether soluble or insoluble polymer would form. The toluene solution of dicyclopentadiene (9) was cooled to -78 °C in a dry ice/isopropanol bath, and the molybdenum catalyst 2, dissolved in a minimum amount of toluene, was transferred to the flask via cannula. The reaction mixture was allowed to warm slowly to room temperature, during which time the polymer remained entirely soluble, as illustrated in Figure 4-7. After precipitation from methanol, the polymer was readily soluble in common organic solvents and was analyzed by GPC and NMR. Although the yield was low, in the range of 20%, it is not unusual to have a large amount of residual monomer present at the conclusion of the polymerization of dicyclopentadiene when monomer concentration is high.[73] Polydicyclopentadiene with a molecular weight of M_n = 28,000 (by GPC) was obtained.



9 11

Figure 4-7. Polymerization of dicyclopentadiene (9) in toluene (2.28 M) at -78 °C with molybdenum catalyst 2.

It is a significant finding that linear, soluble polydicyclopentadiene (11) can be generated at low temperature from a solution concentration that normally leads to crosslinking. If equilibrium ring-opening metathesis of the pendant cyclopentene were responsible for crosslinking, it would be expected that this reaction would be subjected to a ceiling temperature restriction, below which crosslinking occurs. For a solution of dicyclopentadiene in toluene with an initial monomer concentration of 2.28 M, the ceiling temperature must clearly be above 25 °C, since crosslinked product was formed under these conditions. If the mechanism for crosslinking were truly metathesis, one would expect an insoluble product to form below room temperature as well, since reaction conditions would still be below the ceiling temperature. From this standpoint, the formation of a crosslinked polymer cannot be attributed to the metathesis of the pendant cyclopentene. Another source, namely the heat generated from the opening of the norbornene ring, must be responsible for the generation of insoluble products.

The possibility that a floor temperature situation is occurring here for the ring-opening metathesis of the pendant cyclopentene is also very unlikely. The effects of a floor temperature, T_f, are seen for polymerizations where ΔH is very small, and ΔS is endoentropic (ΔS = positive). This rare phenomenon has only been observed in three known cases, for the ring-opening polymerizations of cyclic sulfur octamer, cyclic selenium octamer, and octamethylcyclotetrasiloxane.[52]

The results described here for the solution polymerization of dicyclopentadiene with the molybdenum alkylidene 2, as well as for the polymerization of this monomer at -78 °C, indicate that the heat generated during the ring-opening reaction is sufficient to cause crosslinking in the polymer. The effects of heating were also observed with the model compound, 5,6-dihydrodicyclopentadiene (6), where dimers and trimers were formed solely from heating the compound in the absence of a catalyst. If this heat is somehow removed, either through dilution or by cooling the reaction medium, crosslinking is inhibited, and linear soluble polymer is generated through a pure metathesis mechanism. These results help to prove that the crosslinked, insoluble polymer generated from dicyclopentadiene (9) with molybdenum catalyst 2 could not be formed through metathesis of the cyclopentene moiety.

Solution polymerization with ruthenium alkylidenes

After examining the reactivity of dicyclopentadiene (9) with the molybdenum catalyst 2, the reactivity of this monomer was investigated with the two ruthenium alkylidenes (3 and 4). Initial studies were performed using the tricyclohexylphosphine version of Grubbs' ruthenium alkylidene (3) on bulk samples of dicyclopentadiene, as illustrated in Figure 4-8. The results with this initiator were similar to those found with the molybdenum alkylidene, except that the reaction was much slower, and the physical appearance of the polymer was different. The violet-purple color of the initiator persisted for a few moments, then faded to a dull red-brown before the solution became cloudy and eventually turned entirely opaque. The polymer samples (12) that resulted from these reactions were gray colored, waxy gels that were completely insoluble in common organic solvents.

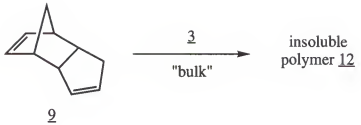


Figure 4-8. Bulk polymerization of dicyclopentadiene (9) with ruthenium alkylidene 3.

The concentration of dicyclopentadiene (9) was varied from "bulk" conditions (enough toluene added to solubilize catalyst) to 1 part dicyclopentadiene per 100 parts toluene in order to determine if crosslinking could be prevented through dilution, as described in Table 4-3. In each of the concentrations that was examined, insoluble polymer gel was formed. This result was quite puzzling, because no exotherm was detected for initiation with the ruthenium alkylidene 3, even at near bulk conditions. Polymerization was in fact rather slow, as compared to the classical system 1 and the molybdenum alkylidene 2, hence it was doubtful that localized heating was responsible for crosslinking in this system.

There are blatant inconsistencies between the results obtained for the solution polymerization of dicyclopentadiene (9) with Schrock's molybdenum alkylidene 2 and those derived from the solution studies presented here with Grubbs ruthenium alkylidene, 3. If crosslinking can be eliminated by dilution or lower reaction temperature for the case of the molybdenum initiator, the same should have held true for the ruthenium catalyst, if this system only initiates metathesis chemistry. The formation of these insoluble gels is

Table 4-3. Results for the polymerization of dicyclopentadiene (9) with ruthenium catalyst 3 at various dilutions.

Concentration[a]	Polymer Condition
"bulk" (7.5 M)	insoluble gel
1:1 (3.51 M)	insoluble gel
1:2 (2.28 M)	insoluble gel
1:5 (1.12 M)	insoluble gel
1:10 (0.60 M)	insoluble gel
1:25 (0.25 M)	insoluble gel
1:50 (0.13 M)	insoluble gel
1:100 (0.07 M)	insoluble gel

[a]Concentrations given in monomer to toluene, w/w.

confusing, especially at a dilution of 1:100 monomer to toluene, since equilibrium metathesis of the fused cyclopentene would be unfavorable under these conditions.

It is well known that the activity of the ruthenium alkylidene is reduced compared to that of the molybdenum catalyst.[49-51] Therefore, it is unlikely that the ruthenium catalyst would be powerful enough to initiate ring-opening metathesis polymerization of a disubstituted cyclopentene when this transformation is not possible with the more reactive molybdenum alkylidene. The polymerization of dicyclopentadiene (9) was also examined with the triphenylphosphine version of Grubbs' catalyst (4), which is even less reactive towards metathesis than its tricyclohexyl analog (3). Again, only insoluble polymer gels were formed at all concentrations examined, as illustrated in Figure 4-9.

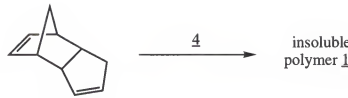


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Figure 4-9. Polymerization of dicyclopentadiene with triphenylphosphine ruthenium catalyst 4.

Some questions are raised from this solution study since insoluble polymers were formed for all monomer concentrations with the ruthenium catalyst 3. Perhaps some type of reaction is occurring in addition to metathesis when this catalyst is employed. In order to test if competing reactions were taking place, such as cationic or radical polymerization, n-propylacetate and *p*-methoxyphenol were added independently to the polymerization of dicyclopentadiene with ruthenium alkylidene 3. Previous work completed by Nubel[98] and Maughon[99] with these compounds has shown them to act as inhibitors for cationic and radical processes without any adverse effects on metathesis polymerization. As indicated in Figure 4-10, these inhibitors had no effect on the polymerization of dicyclopentadiene (9) with ruthenium initiator 3, except to slow the reaction slightly.

The experiments described above indicate that polymerization of dicyclopentadiene with ruthenium alkylidenes 3 and 4 is occurring through a different set of requirements than when molybdenum alkylidene 2 is employed. Although no evidence could be found for any other mechanism, it does not seem possible that a metathesis process is responsible for the formation of insoluble polymer with catalysts 3 and 4. As discussed in Chapter 3, ruthenium catalysts 3 and 4 showed no metathesis activity with 5,6-dihydrodicyclopentadiene (6), even near bulk concentrations of

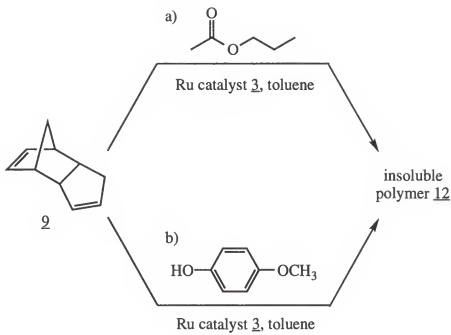


Figure 4-10. Effects of a) n-propylacetate and b) *p*-methoxyphenol on the polymerization of dicyclopentadiene (9) initiated by ruthenium catalyst 3.

monomer. It is also doubtful that localized heating is responsible for the formation of these gels, since the reaction mixture did not exceed room temperature, and formation of the gel was sluggish. Perhaps an alternate mechanism is operating to form these insoluble samples, due to some impurity or contaminant which affects the ruthenium catalyst, or just from the nature of the catalyst itself. The only conclusions that really can be drawn from these experiments are that the molybdenum and ruthenium catalyst systems are quite different, and the ruthenium initiators may induce other chemistry in addition to metathesis.

Crosslinking Studies

The model studies described in Chapter 3 for 5,6-dihydrodicyclopentadiene (6), as well as the findings described above for the polymerization of dicyclopentadiene with the well-defined molybdenum alkylidene 2, suggest that crosslinking does not occur by metathesis in the production of polydicyclopentadiene. Instead, an alternative mechanism, possibly one that is thermally induced, is responsible for the formation of insoluble polymer gels. These conclusions stem from the assumption that the reaction of the pendant cyclopentene through ring-opening metathesis is thermodynamically unfavorable. However, if the thermodynamic parameters of the reaction change during the polymerization, metathesis crosslinking could possibly become allowed.

As discussed previously, ring-opening metathesis is an equilibrium polymerization that is typically driven by the release of ring strain. If a molecule does not possess sufficient ring strain, in comparison to the linear ring-opened polymer, the equilibrium will lie in favor of the reactants, usually resulting in a positive ΔG for the reaction. In cases where ΔH is zero or just slightly negative, high concentrations of monomer are necessary to shift the equilibrium in favor of products. These requirements are imposed on the reaction due to the inherent loss of entropy that is typically associated with polymerization. However, if a point could be reached during a polymerization, termed a critical chain length, where the change in entropy of the system becomes essentially negligible, perhaps metathesis could occur for rings with very little inherent strain, as shown in Figure 4-11. If this were the case, the reaction would not be driven by the enthalpy change of the reaction, but rather by the entropy.

The possibility of crosslinking due to a negligible change in entropy has been suggested for dicyclopentadiene polymerization to explain the results obtained with the well-defined Schrock alkylidene 2.[118] This idea could be feasible if the exact set of

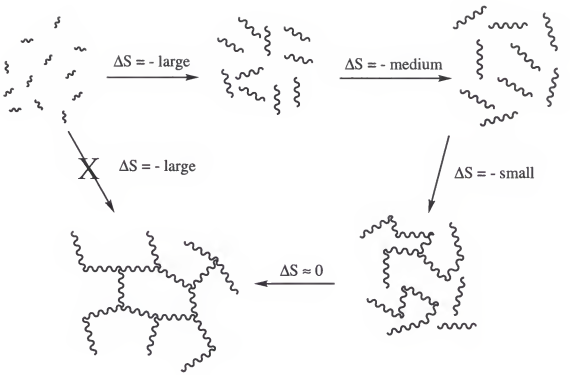


Figure 4-11. Possible crosslinking when ΔS becomes negligible for the ring-opening metathesis of the fused cyclopentene.[118]

conditions, including monomer unit concentration, polymer chain length, and population of active species, could be attained. Three specifically targeted experiments were designed to test the parameters which could lead to thermally induced versus entropy driven crosslinking. The first group involved the formation of linear polydicyclopentadiene in solution, followed by gradual concentration of the solution while an active chain end was present. The second experiment exposed benzaldehyde-capped oligomers of polydicyclopentadiene at various concentrations and molecular weights to the molybdenum alkylidene 2 to see if crosslinking could be induced. Finally, the third set of experiments was based on the idea of the synthesis of a model polymer which could mimic linear polydicyclopentadiene of known molecular weights (i.e. chain

lengths) to explore the possibility and mechanism of crosslinking. In each of these systems, Schrock's molybdenum alkylidene 2 would be used as a metathesis initiator, since the ruthenium alkylidenes 3 and 4 did not yield consistent results between the model studies and the polymerization of dicyclopentadiene.

Gradual Concentration of Linear Polydicyclopentadiene Solution

If a critical concentration of growing polymer chain ends is required from an entropic view for metathesis crosslinking to occur in polydicyclopentadiene, then solutions which are above this concentration should therefore yield insoluble polymer. This theory was tested by generating linear, soluble polydicyclopentadiene in solution under inert conditions, then gradually concentrating the solution under vacuum, as described in Figure 4-12. Since the catalyst should remain active during the concentration of the solution, metathesis crosslinking could be feasible once the critical concentration of growing chains was reached. The solution was slowly evaporated to the point of dryness then exposed to air, which rendered the catalyst inactive for further metathesis. Toluene was added to the flask, and the polymer that had formed dissolved in a matter of minutes, indicating that crosslinking had not occurred. The toluene solution was poured into methanol, and the linear dicyclopentadiene was isolated as a white stringy precipitate.

In a second experiment designed to simulate the heat generated during the exotherm of a dicyclopentadiene polymerization, a solution of dicyclopentadiene and molybdenum catalyst 2 in toluene was prepared under inert conditions and gradually concentrated until the solution volume was decreased to about one third of its original value. At that time, the flask was plunged into an oil bath at 180 °C, and immediate formation of an insoluble gel was observed. After five minutes of heating, the flask was

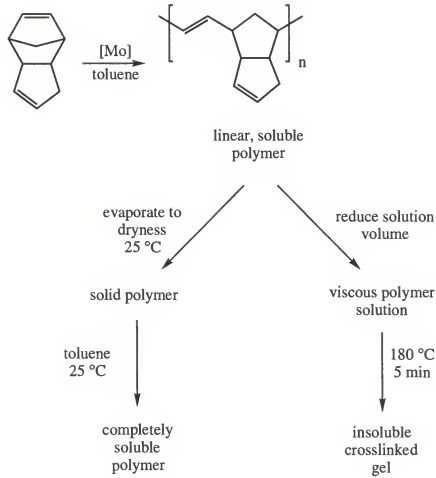


Figure 4-12. Results of gradual concentration of growing polydicyclopentadiene.

cooled to room temperature, opened to the atmosphere, and additional toluene was added. Even with warming the mixture, no appreciable dissolution of the polymer was observed. The polymer was filtered from the toluene, and 1,2,4-trichlorobenzene was added. This mixture was warmed to approximately 150 °C to check the solubility of the polymer. Although the gel was swollen slightly by the solvent, no indication of dissolution was observed. An aliquot of the solution was evaporated, but no polymer residue was obtained.

The results of this study revealed interesting aspects of the formation of polydicyclopentadiene. The gradual concentration of the reaction mixture effectively mimics a series of incremental concentrations, during which time a critical concentration of repeat units and chain ends would have been obtained. At some point during the evaporation of solvent, the concentration of this solution would be equal to the necessary concentration for crosslinking. However, during these experiments, the polymer remained entirely soluble, indicating that even at the maximum concentration of growing chain ends and repeat units, metathesis crosslinking did not occur. Further, if the volume of the solution of growing polymer chains is reduced and this concentrated solution is heated, an insoluble gel forms instantly. These findings support the argument that heating of the solution is responsible for the formation of crosslinked polydicyclopentadiene with the well-defined molybdenum catalyst, rather than an equilibrium concentration or entropy driven metathesis reaction.

Another possible explanation for the formation of insoluble polydicyclopentadiene with the molybdenum alkylidene 2 involves a thermally catalyzed rearrangement to yield a more reactive species for metathesis. As described in Figure 4-13, the linear polymer of *endo*-dicyclopentadiene possesses 1,5-dienes which are in close enough proximity to undergo a Cope rearrangement. The amount of heat released during the formation of the linear polymer should be substantial enough to overcome the activation energy of the rearrangement. The rearranged repeat units would possess an unsaturated 8-membered ring, which would be more reactive for metathesis polymerization than the disubstituted cyclopentene. Ring-opening metathesis polymerization of this cyclooctene would lead to the formation of insoluble polymer. Other experiments can be conducted in this area to explore the feasibility of this rearrangement.

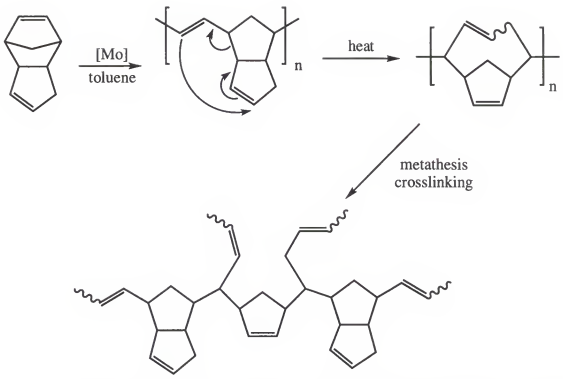


Figure 4-13. Proposed crosslinking of polydicyclopentadiene via Cope rearrangement.

Delayed Crosslinking of Polydicyclopentadiene

Another set of experiments was designed to test the possibility that crosslinking of polydicyclopentadiene may occur through metathesis after a critical chain length or concentration of repeat units is reached. Linear, soluble polydicyclopentadiene was generated and isolated, then exposed independently to the classical catalyst system 1 and the Schrock molybdenum alkylidene 2. Solutions of the linear polymer were made in different concentrations, and examined with each catalyst to determine if crosslinking occurred.

Classical catalysis

Samples of linear, soluble polydicyclopentadiene were generated using Schrock's molybdenum alkylidene 2 in a solution of toluene and endcapped with benzaldehyde. After precipitation and drying of the polymer, the samples were redissolved in various amounts of dry toluene under inert conditions, and the classical catalyst system 1 was added, as illustrated in Figure 4-14. The solutions immediately turned a dark brown and formed tough charred-looking solids. After removing the solid polymer samples from the flask, attempts were made to dissolve the polymers in warm toluene, *o*-xylene, and 1,2,4-trichlorobenzene. All attempts to solubilize these polymers were unsuccessful, indicating

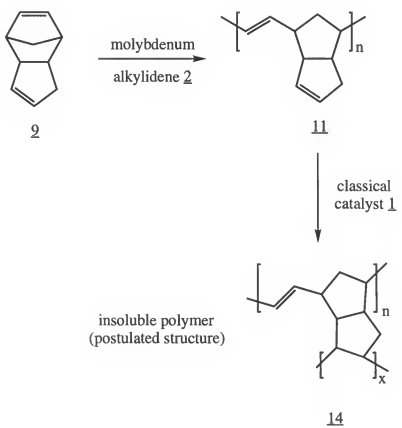


Figure 4-14. Delayed crosslinking of linear polydicyclopentadiene (11) with classical catalyst system 1.

that a crosslinked network may have formed. Since the model compound 5,6-dihydrodicyclopentadiene (6) did not undergo metathesis when exposed to the classical catalyst 1, as discussed in Chapter 3, the mode of crosslinking for this dicyclopentadiene system is also assumed to be an olefin addition process.

Molybdenum alkylidene

Various lengths of polydicyclopentadiene were synthesized and endcapped with benzaldehyde to examine the possibility of delayed crosslinking with the Schrock molybdenum alkylidene 2. The degree of polymerization reported for these oligomers and polymers were determined using calculated values from monomer to initiator ratios and from previously determined catalyst activity. The samples were precipitated from cold methanol, then vacuum dried overnight prior to further reactions with the molybdenum catalyst. The oligomer samples were dissolved in dry toluene in vials under inert conditions, and additional molybdenum alkylidene 2 was added, as described in Figure 4-15. After stirring for 12 hours, the vials were exposed toair and fresh toluene was added. In all cases, as shown in Table 4-4, the polymer samples remained completely soluble, indicating that crosslinking had not occurred.

The findings of this study with molybdenum alkylidene 2 indicate that crosslinking does not occur in solutions of preformed linear polydicyclopentadiene, even where the concentration of repeat units is greater than the limit where insoluble polymers were generated from dicyclopentadiene monomer. No evidence to support metathesis crosslinking has been observed in these systems. In fact, the only crosslinked polymers that were formed from solutions of polydicyclopentadiene were obtained when the preformed linear polymer was exposed to the classical catalyst system (1). As indicated

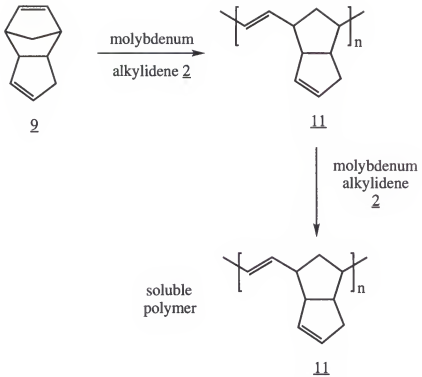


Figure 4-15. Attempted delayed crosslinking of linear polydicyclopentadiene (11) with molybdenum alkylidene 2.

Table 4-4. Delayed crosslinking of dicyclopentadiene oligomers by classical catalyst 1 and molybdenum alkylidene 2.

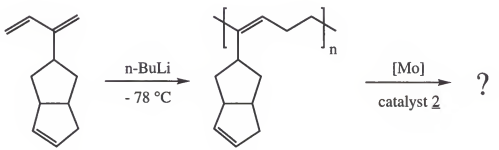
X_n of oligomer[a]	Concentration[b]	Final polymer with 1	Final polymer with 2
45	1 M	insoluble	completely soluble
45	5 M	insoluble	completely soluble
180	1 M	insoluble	completely soluble
180	5M	insoluble	completely soluble
1800	1 M	insoluble	completely soluble

[a]Degree of polymerization calculated from monomer/catalyst ratio.
[b]Concentration based on repeat units/liter of solution.

previously, the insoluble polymer that was generated with the WCl_6/Et_2AlCl system is assumed to have been formed through an olefin addition crosslinking reaction. Both of these results support the hypothesis that the crosslinking mechanism which takes place during the polymerization of dicyclopentadiene is not a metathesis reaction, but rather an olefin addition process that is either chemically or thermally induced.

Delayed Crosslinking of Model Polymer from Anionic Initiation

The final set of experiments that was designed to examine the potential of entropy driven crosslinking involved the design of an isoprene-type monomer, 7-(2-(1,3-butadienyl))bicyclo[3.3.0]oct-2-ene (18). This compound could be polymerized by anionic techniques to yield a mimic of polydicyclopentadiene, as described in Figure 4-16. This monomer would provide an alternate route to a polymer which would contain a similar repeat unit to polydicyclopentadiene, allowing a parallel investigation of the effects of chain length and monomer unit concentration upon crosslinking.



18 19

Figure 4-16. Proposed polymerization of isoprene-type monomer (18), followed by attempted crosslinking with molybdenum alkylidene 2.

One advantage that this polymer system holds over the actual polydicyclopentadiene studies is that a completely different polymerization mechanism forms the polymer backbone. This is a useful comparison since contamination of the polymer by some oxidized or altered form of the molybdenum catalyst 2 could effect the outcome of the crosslinking studies. By utilizing anionic polymerization techniques, a polymer sample can be generated that would be guaranteed to be completely free of molybdenum metal. This way, a clean polymer sample of tailored molecular weight could be generated for study.

The proposed synthesis of this isoprene-type monomer, which involves a series of four reactions based on published literature methods, is outlined in Figure 4-17. The initial reaction (Figure 4-17a) is a condensation of dimethyl 1,3-acetonedicarboxylate with glyoxal to yield the bicyclic diketone (15).[100] This reaction works cleanly to generate white crystals of the desired compound. The second step involves the reduction of the diketone 15 to the diol (16), as shown in Figure 4-17b. Sodium borohydride was chosen as a reducing agent since it is easy to use and accomplished the reaction in a reasonable amount of time. The third step in the reaction scheme is derived from a literature procedure which utilized the pyrolysis of the xanthate ester to yield the bicyclic diene (17).[101] Finally, the compound 17 is converted to the isoprene-type monomer (18) in a one pot reaction which installs the conjugated butadiene unit.[119]

Several attempts were made to complete the synthesis of model compound 18 for crosslinking studies with molybdenum catalyst 2. The reaction scheme was successful through generating the bicyclic diene (17); however, it was not possible to generate enough of this compound to continue with the synthesis of the isoprene-type monomer. With continued efforts in this area, the synthesis of the model monomer 18 should be realized, and crosslinking studies could be conducted.

The synthesis and polymerization of the isoprene-type monomer (18) would allow for the generation of long polymer chains for further attempts at crosslinking. Even so,

based on the results described above for the other crosslinking studies, no metathesis crosslinking would be expected for this system. If one were to speculate about the outcome of crosslinking studies with the isoprene-type polymer (19) with the classical catalyst system 1, it would be reasonable to assume that crosslinking would occur through an olefin addition process. Additionally, if solutions of polymer 19 were heated,

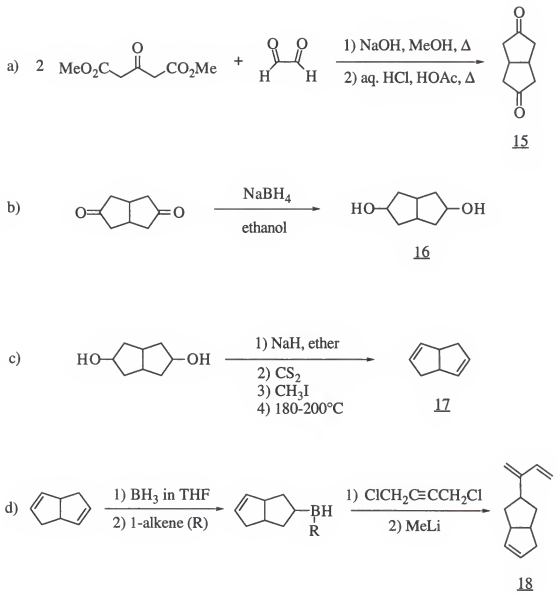


Figure 4-17. Proposed synthesis of the model isoprene-type monomer (18).

it is likely that an insoluble gel would be formed from a thermally induced crosslinking reaction. However, it is postulated that no metathesis crosslinking would be observed with Schrock's molybdenum alkylidene 2, as there have been no results obtained during the preparation of this dissertation that have been consistent with metathesis crosslinking with a well-defined catalyst.

Conclusions

Linear polydicyclopentadiene (11) can be generated in solution with the well-defined molybdenum catalyst 2. However, at higher concentrations of monomer, insoluble material is formed. It is believed that the formation of this material is due to either an olefin addition process or a rearrangement catalyzed by the heat released upon the ROMP of the norbornene subunit of the monomer. An olefin addition process has also been observed with 5,6-dihydrodicyclopentadiene (6), which contains a fused cyclopentene, by thermal exposure without a catalyst present. If the heat is removed from the polymerization of dicyclopentadiene through dilution or by cooling the solution, soluble linear polymer is formed. These results suggests that a thermally catalyzed process is at least partly responsible for the crosslinking reaction that occurs during the polymerization of dicyclopentadiene.

Polymerization of dicyclopentadiene (9) with ruthenium alkylidenes 3 and 4 resulted in the formation of insoluble polymers, regardless of the concentration of the solutions. This finding is inconsistent with the experiments described in Chapter 3 with 5,6-dihydrodicyclopentadiene (6) and the ruthenium catalysts, where no indication of metathesis was observed. The only conclusion that can be drawn from these studies is that chemistry other than metathesis can occur when the ruthenium alkylidenes are employed.

All attempts to crosslink oligomers of linear polydicyclopentadiene with the well-defined molybdenum alkylidene 2 resulted in only the recovery of soluble polymer. With the classical catalyst system 1, insoluble material was obtained, which was assumed to be crosslinked through olefin addition. These results disprove the idea that metathesis crosslinking can be induced by a critical chain length or concentration of polydicyclopentadiene. On the contrary, no indication of metathesis crosslinking was observed whatsoever for these polymerization systems.

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BIOGRAPHICAL SKETCH

Tammy Ann Davidson was born on November 8, 1969, in Columbus, Ohio. She grew up at Buckeye Lake, Ohio, with her parents, Jack and Sherry, and her sister, Cindy. Tammy graduated as valedictorian from Lakewood High School in 1988, and moved down the road to Granville, Ohio, to attend Denison University. While at Denison, she used her free time to study photography and play bassoon in the Heisey Wind Ensemble. Tammy earned her Bachelor of Science degree in chemistry, and graduated in May of 1992. In August 1992, she headed south for a long winter, and began her graduate studies at the University of Forida in the field of organic/polymer chemistry under the expert guidance of Dr. Kenneth B. Wagener. Tammy received her Ph.D. in June 1997, then journeyed with her dog, Moly, to Chapel Hill, North Carolina, for a postdoctoral experience in the group of Dr. Joseph DeSimone at UNC - Chapel Hill.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Kenneth B. Wagener, Chairman
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

John R. Reynolds
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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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